The Oxidation Reaction of Tl(I) to Tl(III) by the Peroxodisulfate Ion. I. Kinetics and Mechanism in an Aqueous Solution

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The oxidation reaction of the thallium(I) ion to the thallium(III) ion by the peroxodisulfate ion has been studied in an aqueous acidic solution. The reaction constituted a chain reaction initiated by the thermal decomposition of the peroxodisulfate ion, the reaction involving no direct reactions between the thallium(I) and peroxodisulfate ions. At thallium(I) ion concentrations larger than 0.004 mol dm^{-3}, the reaction mechanism was assumed to be: $S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-}$; $S_2O_8^{2-} + H^+ \xrightarrow{k_2} HSO_4^- + \frac{1}{2}O_2 + SO_3$; $Tl(I) + SO_4^{\cdot-} \xrightarrow{k_3} Tl(II) + SO_4^{2-}$; $S_2O_8^{2-} + Tl(II) \xrightarrow{k_4} Tl(III) + SO_4^{\cdot-} + SO_4^{2-}$; $2Tl(II) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Tl(I) + Tl(III)$. The rate of the reaction was described as $-d[S_2O_8^{2-}]/dt = (k_1 + k_2[H^+])[S_2O_8^{2-}] + k_4(k_1/k_5)^{1/2}[S_2O_8^{2-}]^{3/2}$. The rate constants at an ionic strength of 0.16 mol dm^{-3} were determined to be $k_1 = 1.99 \times 10^{19} \exp[-157 \text{ kJ mol}^{-1}/RT]\text{s}^{-1}$, $k_2 = 2.75 \times 10^{12} \exp[-103 \text{ kJ mol}^{-1}/RT] \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_4(k_1/k_5)^{1/2} = 2.81 \times 10^{13} \exp[-108 \text{ kJ mol}^{-1}/RT] \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ in 0.01 mol dm^{-3} perchloric acid, the k_4 value being increased with a decrease in the hydrogen-ion concentration. The ionic strength (μ) dependence was described as $\log k_4(k_1/k_5)^{1/2} = -4.17 - 1.05\,\mu^{1/2}$ in 0.01 mol dm^{-3} perchloric acid at 40 °C. The reaction rate was completely retarded by the addition of 1% acrlyronitrile, 5×10^{-6} mol dm^{-3} cerium(III) sulfate, 1×10^{-3} mol dm^{-3} cerium(IV) sulfate, or 0.1 mol dm^{-3} sodium acetate, and it was also remarkably retarded by the addition of 1×10^{-3} mol dm^{-3} tetranitromethane. The copper(II) ion and molecular oxygen did not appreciably affect the reaction rate, but the iron(III) ion accelerated it greatly.

The peroxodisulfate ion is known as a powerful two-electron oxidizing agent, and the oxidation reactions of the organic and inorganic substrates by the peroxodisulfate ion have been extensively studied by a number of researchers and have been reviewed by House,[1] Wilmarth and Haim,[2] Wilson,[3] and Buist.[4] However, the investigation of the oxidation reaction of the thallium(I) ion by the peroxodisulfate ion has not been done previously. Bednar[5] studied the induced oxidation of the thallium(I) ion by the iron(II) ion-hydrogen peroxide reaction and concluded that the thallium(II) ion is formed as an intermediate by the reaction with the hydroxyl radical. The reaction of thallium(I) with the hydroxyl radical giving the thallium(II) ion also occurs during the photolysis[6] and radiolysis[7] of cerium(IV)-thallium(I) mixtures. It is now believed that the thallium(II) ion exists as an intermediate in the redox reaction of the thallium(I)-thallium(III) couple. In the oxidation reaction of the thallium(I) ion to the thallium(III) ion by the peroxodisulfate ion, three schemes for the reaction can be tentatively assumed: (1) a single step of the two-electron transfer by the direct reaction between the thallium(I) and peroxodisulfate ions; (2) two successive reactions of the one-electron transfer, involving the thallium(II) ion as the intermediate species, and (3) a reaction initiated only by the thermal decomposition of the peroxodisulfate ion, without any direct reactions between the reactants. The present paper intends to characterize each scheme and to ascertain the true mechanism of the reaction.

Experimental

Chemicals. Reagent-grade potassium peroxodisulfate of the Wako Pure Chemicals Co., Inc., was recrystallized twice from redistilled water and dried at 25 °C in a vacuum desiccator. Thallium(I) perchlorate was prepared by dissolving thallium(I) sulfate in a perchloric acid solution, recrystallizing it from an aqueous perchloric acid solution, washing it with ethanol, and drying it at 80 °C in a vacuum-drying oven. The thallium(I) perchlorate was confirmed to be free of sulfate ions. The sodium perchlorate used for adjusting the ionic strength was recrystallized twice from the redistilled water. The thallium(III) perchlorate was prepared by dissolving Tl_2O_3 in about 5 mol dm^{-3} perchloric acid at 60—70 °C for several hours. All the other chemicals used were guaranteed reagents. The redistilled water was prepared from the anion- and cation-exchange resin water by successive distillations from solutions with and without permanganate in a glass still.

Procedure. Most of the experiments were carried out in a solution of 0.1 mol dm^{-3} sodium perchlorate and 0.01 mol dm^{-3} perchloric acid at 40 °C; no buffer solutions were used in any experiments. The reaction vessel was covered with black adhesive-plastic tape to ensure darkness, and was placed in a thermostat bath. The aliquot samples were withdrawn at appropriate times and mixed with a cold solution of 1% acrylonitrile, so that the reaction was almost completely stopped and the temperature of the solution was reduced to about 25 °C. Then the concentrations of the peroxodisulfate and thallium(I) ions remaining were measured by means of polarography. The thallium(I)-ion concentration was determined by means of a.c. polarography at −0.45 V *vs.* SCE in a solution of 0.01 mol dm^{-3} perchloric acid, 0.1 mol dm^{-3} sodium perchlorate, and 0.01% gelatine at 25 °C. After the separation of the thallium(III) ion formed from the peroxodisulfate ion by filtering it through the cation-exchange resin, the peroxodisulfate-ion concentration was determined by means of d.c. polarography at 0.2 V *vs.* SCE in a solution with the same constituents as in the measurement of the thallium(I)-ion concentration. The method of the polarographic determination for the peroxodisulfate-ion concentration is essentially the same as that used in the previous studies.[8,9] The concentration of the thallium(III) ion formed was determined as follows. All the thallium(I) ion remaining in the reacting solution was once precipitated by the addition of a slight excess of CrO_4^{2-} in an acetate buffer solution with a 4.8 of pH. After the separation of the thallium(I) ion as Tl_2CrO_4, the thallium

(III) ion in the filtered solution was precipitated as $Tl(OH)_3$ in 0.1 mol dm^{-3} sodium hydroxide. The sediment of the hydroxo thallium(III) after filtration was dissolved in a perchloric acid solution. Then, the thallium(III)-ion concentrations were determined by means of d.c. polarography at 0.2 V *vs.* SCE under the conditions used for the measurements of the concentrations of the peroxodisulfate and thallium(I) ions. Blank experiments with mixtures of peroxodisulfate, thallium(I), and thallium(III) ions of the same constitutions as those in the reaction mixtures showed that this method of determination yields reliable results. It was also confirmed that no appreciable reaction of the peroxodisulfate ion with the thallium(I) ion occurred during the procedures for the determination of the concentrations.

Results

Stoichiometry. With concentrations of 8.0×10^{-3} mol dm^{-3} in potassium peroxodisulfate and 8.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate, the concentrations of both peroxodisulfate and thallium(I) ions disappearing due to the reaction were determined and the results are shown in Table 1. The results in Table 1 indicate that, at the initial stages of reaction, the concentrations of the peroxodisulfate ion disappearing are almost equivalent to those of the thallium(I) disappearing, and that, at the later stages of reaction, those of the peroxodisulfate ion disappearing become larger than those of the thallium(I) ion disappearing. With 1.6×10^{-2} mol dm^{-3} in potassium peroxodisulfate and 4.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate, the concentration of the peroxodisulfate ion disappearing and that of the thallium(III) ion being formed were determined and the results are shown in Table 2. At the initial stages of reaction, the concentrations of the peroxodisulfate ion disappearing are almost equivalent to those of the thallium(III) ion being formed, and, according to the progress of the reaction, those of the peroxodisulfate ion disappearing become larger than those of the thallium(III) ion being formed.

Table 1. Stoichiometry[a)]

Reaction time h	$[S_2O_8^{2-}]_{disapp.}$ 10^{-3} mol dm^{-3}	$[Tl(I)]_{disapp.}$ 10^{-3} mol dm^{-3}	$[S_2O_8^{2-}]_{disapp.}$[b)] 10^{-3} mol dm^{-3}
0.5	0.06	0.07	0.02
5	0.67	0.61	0.08
21	1.92	1.75	0.31
47	3.40	2.74	0.43
70	4.16	3.25	0.60
94	4.80	4.02	0.85
119	5.34	4.34	1.05
149	5.82	4.78	1.30

a) Initial concentrations of 8.0×10^{-3} mol dm^{-3} for both potassium peroxodisulfate and thallium(I) perchlorate, 0.01 mol dm^{-3} in perchloric acid, and 0.1 mol dm^{-3} in sodium perchlorate; 40 °C; dark. b) As in a), but in the absence of thallium(I).

Table 2.

Reaction time h	$[S_2O_8^{2-}]_{disapp.}$ 10^{-3} mol dm^{-3}	$[Tl(III)]_{formed}$ 10^{-3} mol dm^{-3}
1	0.35	0.38
2	0.70	0.70
3	1.05	1.1
4	1.42	1.3
5	1.67	1.6

a) Condition as in Table 1; except for 1.6×10^{-2} mol dm^{-3} in potassium peroxodisulfate, 4.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate, and an ionic strength of 0.06 mol dm^{-3}.

Reaction Order and Rate Law. The initial rate of the reaction (V_i) was determined at varied concentrations of the thallium(I) and peroxodisulfate ions under given conditions. The results are shown in Figs. 1 and 2. The plot of V_i *vs.* $[Tl(I)]_i$ in Fig. 1 indicates that the rate of the reaction increases linearly

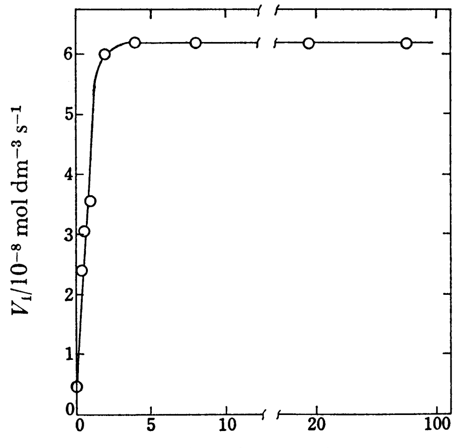

Fig. 1. Plot of V_i *vs.* $[Tl(I)]_i$.
Conditions as in Table 3; except varied concentrations of thallium(I) perchlorate.

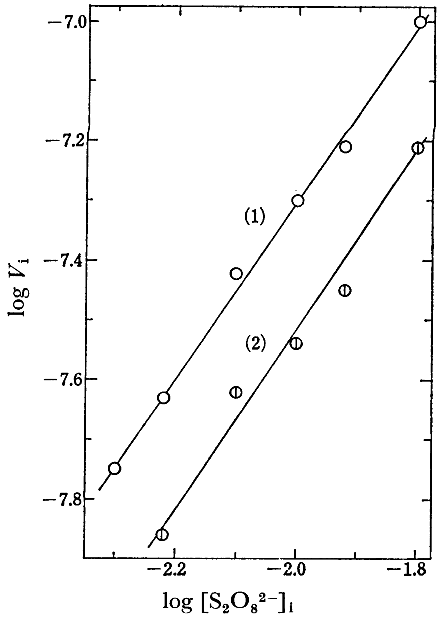

Fig. 2. Plot of log V_i *vs.* log $[S_2O_8^{2-}]_i$.
Conditions as in Table 3; except varied concentrations of potassium peroxodisulfate, and ionic strengths 0.06 and 0.16 mol dm^{-3} for lines 1 and 2, respectively.

with an increase in the thallium(I)-ion concentrations for the low concentrations, and that it then becomes independent of the thallium(I) ion over the range from 0.004 to 0.08 mol dm^{-3}. The plot of log V_i *vs.* log $[S_2O_8^{2-}]_i$ in Fig. 2 shows a straight line with a slope of 1.5±0.1. Those two results indicate that the rate of reaction between thallium(I) and peroxodisulfate ions at concentrations larger than 0.004 mol dm^{-3} thallium(I) is of zero and 1.5 order with respect to the concentrations of thallium(I) and peroxodisulfate ions respectively. Thus, the rate of reaction obeys Eqs. 7 and 9 (*vide infra*).

Effect of Radical Scavengers. The influence of the radical scavengers on the rate of reaction was examined, the results are shown in Table 3. The addition of 1% acrylonitrile completely inhibited the reaction rate, with the production of some amounts of a white sediment of polyacrylonitrile, indicating the existence of $SO_4^{\overline{\cdot}}$ and/or OH· radicals in the reacting solutions. Both the cerium(III) and cerium(IV) ions were very strong retarders of the reaction, even 5×10^{-6} mol dm^{-3} cerium(III) or 1×10^{-3} mol dm^{-3} cerium(IV) being able to reduce the reaction rate to the rate of the thermal decomposition of the peroxodisulfate ion. This clearly indicates the existence of both the oxidizing and reducing radicals in the reacting solution. Tetranitromethane was also a strong retarder of the reaction, indicating the existence of a thallium(II) species which can be act as a reducing agent for tetranitromethane. The acetate ion was also a retarder of the reaction, the reaction being completely inhibited by the addition of 0.1 mol dm^{-3} acetate. On the contrary, the iron(III) ion was an accelerator, and the copper(II) ion hardly affected the rate of reaction.

Acidity Dependence. The rate of the thermal decomposition of peroxodisulfate increased with an increase in the acidity of the reaction solution, while the rate of reaction between peroxodisulfate and thallium(I) ions decreased with an increase in the acidity. The results are tabulated in Table 4. The pH in the reacting solution become smaller according to the progress of reaction; this was because of the hydrolysis of the thallium(III) ion formed, *i.e.*, $H_2O+Tl^{3+}\rightarrow TlOH^{2+}+H^+$. However, the pH buffer solution was not used because most buffers may affect the reaction rate much as the acetate ion affects the rate of reaction (see Table 3).

Temperature Dependence. First, the rate of the thermal decomposition of the peroxodisulfate ion was

Table 3. Influence of radical Scavengers[a]

Radical scavengers	V_i/10^{-8} dm^{-3} mol s^{-1}
None	6.17
None	6.00 (in N_2 saturated)
None	0.45 (in the absence of Tl(I))
1% acrylonitrile	0.53[b] (in the absence of Tl(I))
1% acrylonitrile	0.61[b]
1×10^{-3} mol dm^{-3} tetranitromethane	2.50
1×10^{-6} mol dm^{-3} cerium(III)	3.56
5×10^{-6} mol dm^{-3} cerium(III)	0.44
1×10^{-5} mol dm^{-3} cerium(III)	0.40
1×10^{-4} mol dm^{-3} cerium(III)	0.47
1×10^{-4} mol dm^{-3} cerium(IV)	1.45
1×10^{-3} mol dm^{-3} cerium(IV)	0.72
1×10^{-4} mol dm^{-3} copper(II)	6.95
1×10^{-3} mol dm^{-3} copper(II)	7.12
1×10^{-4} mol dm^{-3} iron(III)	14.7
1×10^{-3} mol dm^{-3} iron(III)	19.7
0.01 mol dm^{-3} CH_3COONa	1.67 (pH 6.35)
0.01 mol dm^{-3} CH_3COONa	1.55 (pH 1.7 with 0.1 mol dm^{-3} $HClO_4$)
0.1 mol dm^{-3} CH_3COONa	0.4 (pH 2.4 with 0.1 mol dm^{-3} $HClO_4$)
0.2 mol dm^{-3} CH_3COONa	0.2 (pH 4.62 with 0.1 mol dm^{-3} $HClO_4$)

a) Initial concentrations of 0.016 mol dm^{-3} in potassium peroxodisulfate, 4.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate, 0.01 mol dm^{-3} in perchloric acid, and 0.1 mol dm^{-3} sodium perchlorate; 40 °C; dark. b) A white sediment of polyacrylonitrile was formed in the reacting solution, irrespective of the presence or absence of the thallium(I) ion.

Table 4. Influence of the acidity[a]

$[HClO_4]_{added}$	pH[c]	V_i	V_i'	k_b	k_4[b]
mol dm^{-3}		10^{-8} dm^{-3} mol s^{-1}	10^{-8} dm^{-3} mol s^{-1}	10^{-5} dm$^{3/2}$ mol$^{-1/2}$ s^{-1}	10^3 dm^3 mol^{-1} s^{-1}
0.1		4.28	2.82	0.72	0.54
0.05	1.32—1.3	3.55	1.50	1.01	0.75
0.02	1.72—1.68	5.00	0.71	2.12	1.58
0.01	1.97—1.84	6.17	0.45	2.83	2.11
0.005	2.23—2.00	6.17	0.32	2.89	2.16
0.002	2.73—2.26	8.45	0.24	4.06	3.03
0	7 —2.34	10.3	0.10	5.04	3.76

a) Conditions as in Table 3, except for the varied concentrations of perchloric acid. V_i and V_i' indicate the initial rate of the decomposition of the peroxodisulfate ion in the presence and in the absence of the thallium(I) ion respectively. b) k_4 calculated by the relationship of $k_b=k_4(k_1/k_5)^{1/2}$ with $k_1=1.15\times10^{-7}$ s^{-1} and $k_5=6.4\times10^8$ dm^3 mol^{-1} s^{-1} at 40 °C. The k_5 was obtained from the data reported by Falcinella *et al.*[14] of 5.5×10^8 dm^3 mol^{-1} s^{-1} at 25 °C, with an activation free energy of 7.9 kJ mol^{-1}. c) The pH range indicates the pH changes at the time of reaction over the range from 0 to 5 h, for which the initial rate, V_i, has been determined.

TABLE 5. TEMPERATURE DEPENDENCE OF THE RATE OF THERMAL DECOMPOSITION OF THE PEROXODISULFATE ION[a)]

Temp	0.01 mol dm^{-3} NaOH	0.01 mol dm^{-3} HClO$_4$	
°C	k_a/10^{-7} s^{-1}	k_a/10^{-7} s^{-1}	k_2/10^{-5} dm^3 mol^{-1} s^{-1}
40	1.15	2.8	1.65
45	3.45	7.95	4.5
50	8.70	14.8	6.1
55	18.5	27.7	9.2

a) 0.016 mol dm^{-3} in potassium peroxodisulfate, 0.1 mol dm^{-3} in sodium perchlorate, and 0.01 mol dm^{-3} in sodium hydroxide or 0.01 mol dm^{-3} in perchloric acid; varied temperatures; dark; $k_a=k_1+k_2[H^+]$.

TABLE 6. TEMPERATURE DEPENDENCE OF THE RATE OF THE REACTION OF THE PEROXODISULFATE ION WITH THE THALLIUM(I) ION[a)]

Temp	V_i	V_i'	k_b
°C	10^{-8} dm^{-3} mol s^{-1}	10^{-8} dm^{-3} mol s^{-1}	10^{-5} dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
30	1.83	—	0.91
35	2.22	—	1.10
40	6.17	0.45	2.83
45	11.4	1.3	5.00
50	21.8	2.4	9.60
55	38.0	4.4	16.6

a) Conditions as in Table 4, except for 0.01 mol dm^{-3} perchloric acid and varid temperatures.

measured in 0.01 mol dm^{-3} sodium hydroxide and 0.01 mol dm^{-3} perchloric acid at an ionic strength of 0.16 mol dm^{-3} and at temperatures from 40 to 55 °C. Using the relationship of $-d[S_2O_8^{2-}]/dt=(k_1+k_2[H^+])[S_2O_8^{2-}]$ which has been reported by Kolthoff and Miller,[10)] the values of k_1 and k_2 were evaluated to be as shown in Table 5. The activation energies for the k_1- and k_2-reactions were, respectively, 157 kJ mol^{-1} and 103 kJ mol^{-1}, the values being in good agreement with the 140 kJ mol^{-1} and 109 kJ mol^{-1} of the corresponding reactions reported by Kolthoff and Miller.[10)] Next, the rate of the decomposition of the peroxodisulfate ion in the presence of the thallium(I) ion was measured in 0.01 mol dm^{-3} perchloric acid at an ionic strength of 0.16 mol dm^{-3} and at temperatures over the range from 30 to 55 °C (Table 6). The plot of ln k_b *vs.* T^{-1} gave a straight line, the k_b being described as $k_b=2.81\times10^{13}\exp[-108\text{ kJ mol}^{-1}/RT]$ dm$^{3/2}$ mol$^{-1/2}$ s^{-1}.

Ionic-strength Dependence. With concentrations of 1.6×10^{-2} mol dm^{-3} in potassium peroxodisulfate, 4.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate, and 0.01 mol dm^{-3} perchloric acid, and with varied concentrations of sodium perchlorate at 40 °C, the initial rates of the disappearance of peroxodisulfate were 9.7×10^{-8}, 8.0×10^{-8}, 6.2×10^{-8}, 5.7×10^{-8}, and 5.2×10^{-8} dm^{-3} mol s^{-1} at ionic strengths of 0.06, 0.11, 0.16, 0.21, and 0.26 mol dm^{-3} respectively. The rate decreased with an increase in the ionic strength (μ), the plot of log k_b *vs.* $\mu^{1/2}$ being rectilinear with a slope of -1.05.

Discussion

The results of Fig. 1 and Table 3 absolutely deviated the schemes, 1 and 2, which were mentioned in the introduction section, but they could be well accounted for by Scheme 3, in which there are no direct reactions between peroxodisulfate and thallium(I) ions. Moreover, all the results obtained could be accounted for by the following reaction mechanism:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{-\cdot}\ \text{[Initiation]} \qquad (1)^{10)}$$

$$S_2O_8^{2-} + H^+ \xrightarrow{k_2} HSO_4^- + \frac{1}{2}O_2 + SO_3 \qquad (2)^{10)}$$

$$\text{Tl(I)} + SO_4^{-\cdot} \xrightarrow{k_3} \text{Tl(II)} + SO_4^{2-} \qquad (3)$$

$$S_2O_8^{2-} + \text{Tl(II)} \xrightarrow{k_4} \text{Tl(III)} + SO_4^{-\cdot} + SO_4^{2-} \qquad (4)$$

$$2\text{Tl(II)} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{Tl(I)} + \text{Tl(III)}\ \text{[Termination]} \qquad (5)^{11)-14)}$$

Reactions 3 and 4 constitute a chain reaction in which Reaction 1 is the initiation reaction. The most probable termination reaction is a disproportionation of the thallium(II) ion. Schwarz *et al.*[11)] reported the values for k_5 and k_{-5} to be 1.9×10^8 and 7.5×10^{-25} dm^3 mol^{-1} s^{-1} respectively in 1 mol dm^{-3} perchloric acid. Therefore, the backward reaction of Reaction 5 could actually be negligible. Thus, neglecting the backward reaction, and assuming steady-state concentrations for $SO_4^{-\cdot}$ and Tl(II), the following equations are derived:

$$[\text{Tl(II)}] = \sqrt{\frac{k_1[S_2O_8^{2-}]}{k_5}};$$

$$[SO_4^{-\cdot}] = \frac{2k_1[S_2O_8^{2-}]+k_b[S_2O_8^{2-}]^{3/2}}{k_3[\text{Tl(I)}]} \qquad (6)$$

$$-d\,[S_2O_8^{2-}]/dt = k_a[S_2O_8^{2-}] + k_b[S_2O_8^{2-}]^{3/2} \qquad (7)$$

$$-d\,[\text{Tl(I)}]/dt = k_1[S_2O_8^{2-}] + k_b[S_2O_8^{2-}]^{3/2} \qquad (8)$$

where $k_a=k_1+k_2[H^+]$ and $k_b=k_4(k_1/k_5)^{1/2}$.
The first term on the right-hand side of Eq. 7 corresponds to the termal decomposition of the peroxodisulfate ion itself, and it is, except in a stlongly acidic

solution, much smaller than the second term (*e. g.*, see Fig. 1). When the first term on the right-hand side of Eq. 7 is negligible. Eqs. 9 and 10 are derived:

$$-\mathrm{d}\,[S_2O_8^{2-}]/\mathrm{d}t = k_b[S_2O_8^{2-}]^{3/2} \tag{9}$$

By integrating Eq. 9, we obtain:

$$\frac{1}{\sqrt{[S_2O_8^{2-}]}} = \frac{k_b}{2}t + \frac{1}{\sqrt{[S_2O_8^{2-}]_i}} \tag{10}$$

It may be seen from Fig. 3 that the relationship of Eq. 10 is experimentally satisfied, the slope in the plot of $[S_2O_8^{2-}]^{1/2}$ *vs.* t being unaffected by the initial concentrations of both the thallium(I) ion and the peroxodisulfate ion. The slight deviation from the straight line might be attributable to the first term of $k_a[S_2O_8^{2-}]$ in Eq. 7.

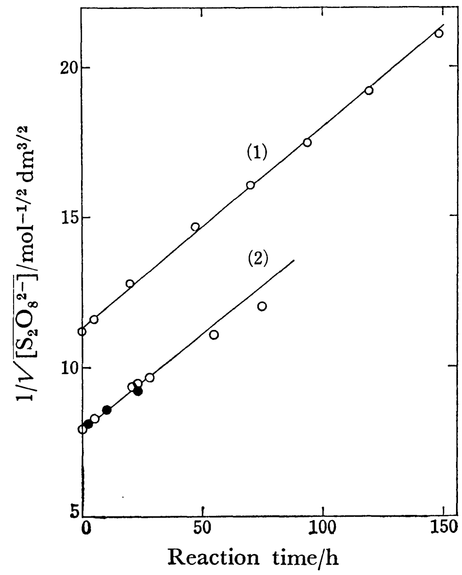

Fig. 3. Plot of $[S_2O_8^{2-}]^{-1/2}$ *vs.* t.
Conditions for line 1 are the same as in *a*) of Table 1 and those of line 2 are 1.6×10^{-2} mol dm^{-3} in potassium peroxodisulfate, 8.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate for the plot ○, and 4.0×10^{-3} mol dm^{-3} in thallium(I) perchlorate for the plot ●. The other conditions are the same as in line 1.

The fact that the concentrations of the peroxodisulfate ion disappearing were larger than those of thallium(I) disappearing in Table 1 is due to the non-radical decomposition of the peroxodisulfate ion of Eq. 2. Thus, Eq. 7 is larger by the $k_2[H^+]\,[S_2O_8^{2-}]$ than Eq. 8. Reaction 3 is a reaction between the thallium(I) ion and the $SO_4^{\overline{\cdot}}$ radical. Therefore, when the thallium(I) ion concentration is extremely low, the rate of the whole reaction is controlled by Reaction 3, the rate being dependent on the thallium(I)-ion concentrations. This could, in practice, be observed at concentartions smaller than 2.0×10^{-3} mol dm^{-3} of thallium(I) (Fig. 1). Since the rate of Reaction 3 becomes slow at such low concentrations of the thallium(I) ion, Reactions 11 to 14 may occur together with Reactions 1 to 5, the reactions competing with each other:

$$H_2O + SO_4^{\overline{\cdot}} \rightleftharpoons HSO_4^- + OH\cdot \tag{11}$$ [10,16]

$$Tl(I) + OH\cdot \longrightarrow Tl(II) + OH^- \tag{12}$$ [15]

$$Tl(II) + OH\cdot \longrightarrow Tl(III) + OH^- \tag{13}$$

$$Tl(II) + SO_4^{\overline{\cdot}} \longrightarrow Tl(III) + SO_4^{2-} \tag{14}$$

The reaction mechanism at low concentrations of the thallium(I) ion is thought to be basically equivalent to that at the higher concentrations of the thallium(I) ion. When the thallium(I) ion concentrations were so high that Reaction 3 could be fast enough, Reactions 11 and 14, and accordingly all the reactions from 11 to 14, would be eliminated from the reaction scheme because the concentrations of $SO_4^{\overline{\cdot}}$ at the steady states are extremely low under such conditions. The strong inhibiting effect of acrylonitrile on the reaction rate, with a production of polyacrylonitrile, indicates that the chain-reaction mechanism is initiated by a radical. The inhibiting effect of the cerium(III) ion is due to the competitive reactions, 15 and 16, with Reactions 3, 4, and 5:

$$Ce(III) + SO_4^{\overline{\cdot}} \xrightarrow{k_{15}} Ce(IV) + SO_4^{2-} \tag{15}$$ [17]

$$Ce(III) + Tl(II) \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} Ce(IV) + Tl(I) \tag{16}$$ [18]

Since the chain reaction in 4.0×10^{-3} mol dm^{-3} thallium(I) was completely inhibited by the addition of 5×10^{-6} mol dm^{-3} cerium(III), the rates of Reactions 15 and 16 are thought to be much faster than those of Reactions 3 and 4. The standard reduction potentials for the $Tl^{2+}+e^- \rightleftharpoons Tl^+$ and $Ce^{4+}+e^- \rightleftharpoons Ce^{3+}$ are 2.22 V[14] and 1.61 V[19] respectively at 25 °C. Therefore, Reaction 16 occurs very much towards the right, with an equilibrium constant of $\log K_{16}=10.9$. Thus, the rate constant k_{16} is estimated to be 9×10^5 dm^3 mol^{-1} s^{-1} by using the equilibrium constant with $k_{-16}=4.7\times10^{-5}$ dm^3 mol^{-1} s^{-1} at 50 °C.[18] The k_{16} value estimated is some hundreds times larger than the k_4 value. The cerium(IV) ion was also a strong retarder of the reaction between peroxodisulfate and thallium(I) ions. The inhibiting effect of the cerium(IV) ion is attributable to the occurrence of Reaction 17, which can be followed by Reactions 15 and 16:

$$Ce(IV) + Tl(II) \rightleftharpoons Ce(III) + Tl(III) \tag{17}$$

Since the standard reduction potential for the reaction of $Tl^{3+}+e^- \rightleftharpoons Tl^{2+}$ is 0.33 ± 0.05 V[14] at 25 °C, Reaction 17 occurs towards the extreme right-hand side, with an equilibrium constant of $\log K_{17}=21.7$. Tetranitromethane is an excellent electron-acceptor. Therefore, the inhibiting effect of tetranitromethane is attributable to the occurrence of Reaction 18, which competes with Reactions 4 and 5:

$$Tl(II) + C(NO_2)_4 \xrightarrow{k_{18}} Tl(III) + C(NO_2)_3^- + NO_2 \tag{18}$$

$k_{18} = 4\times10^8$ dm^3 mol^{-1} s^{-1} at pH 8—9[13]

The acceleration effect of the iron(III) ion could be due to the occurrence of Reactions 19, 20, and 21:

$$Tl(II) + Fe(III) \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} Tl(III) + Fe(II) \tag{19}$$

$$Tl(II) + Fe(II) \xrightarrow{k_{20}} Tl(I) + Fe(III) \tag{20}$$

$$S_2O_8^{2-} + Fe(II) \xrightarrow{k_{21}} Fe(III) + SO_4^{-\cdot} + SO_4^{2-} \quad (21)$$

Schwarz *et al.*[11] reported the k_{19}, k_{-19}, and k_{20} to be 3.4×10^5, 0.0139, and 6.7×10^6 dm^3 mol^{-1} s^{-1} respectively in 1 mol dm^{-3} perchloric acid at 23 °C . The forward reactions of Eqs. 19 and 20 are competitive with Reactions 4 and 5. The rate constant k_{21} at 25 °C is 141 dm^3 mol^{-1} s^{-1} [20] and 25 dm^3 mol^{-1} s^{-1} [21] at an ionic strength of zero and 0.1 mol dm^{-3} respectively. Thus, the k_{21} value is somewhat smaller than the k_4 in Table 4. Nevertheless, the iron(III) ion greatly accelerated the reaction between peroxodisulfate and thallium(I) ions. By the addition of the iron(III) ion, the chain reaction may be carried out by Reactions 3, 4, 19, and 21, the chain termination being Reaction 20 in place of Reaction 5. The occurrence of Reactions 19 and 21, accompanied by the diminution in the termination Reaction 5, is thought to be a probable cause of the acceleration effect of the iron(III) ion. In the presence of the copper(II) ion, the equilibrium Reaction 22 will hold.

$$Tl(II) + Cu(II) \rightleftharpoons Tl(III) + Cu(I) \quad (22)$$

The equilibrium of Eq. 22 occurs towards the extremely left-hand side, with an equilibrium constant of log $K_{22} = -3$, the value being calculated by means of the redox potentials of 0.33 V[14] and 0.153 V[19] for the Tl^{3+}/Tl^{2+} and Cu^{2+}/Cu^{+} couples respectively. The rate constant for the reaction of $S_2O_8^{2-} + Cu(I) \rightarrow Cu(II) + SO_4^{-\cdot} + SO_4^{2-}$ has been reported to be 1.4×10^3 dm^3 mol^{-1} s^{-1} in 1 mol dm^{-3} KCl at 25 °C:[22] the value is almost the same magnitude as the k_4 values. The two conclusions above lead to the conclusion that the copper(II) ion could not be an effective accelerator for the reaction between peroxodisulfate and thallium(I) ions. The rate of the reaction between peroxodisulfate and thallium(I) ions decreased with an increase in the acidity in the reacting solution, whereas the rate of the thermal decomposition of the peroxodisulfate ion increased with an increase in the acidity (Table 4). Considering the relationship of Eq. 7, equation 23 may be assumed:

$$V_i = V_i' + k_b[S_2O_8^{2-}]_i^{3/2} \quad (23)$$

where V_i and V_i' indicate the initial rate of the disappearance of the peroxodisulfate ion in the presence and in the absence of the thallium(I) ion respectively. Equation 23 is satisfied, at least for the initial stages of reactions. The values of k_b and k_4 in Tables 4 and 6 where estimated by using Eq. 23 with the relatioship of $k_b = k_4(k_i/k_5)^{1/2}$. The pH dependence of k_4 may be attributable to the simultaneous reactions of $Tl^{2+}(aq)$ and $Tl(OH)^+$ with the peroxodisulfate ion.

$$S_2O_8^{2-} + Tl^{2+}(aq) \xrightarrow{k_{4a}} Tl(III) + SO_4^{-\cdot} + SO_4^{2-} \quad (4a)$$

$$S_2O_8^{2-} + TlOH^+ \xrightarrow{k_{4b}} Tl(III) + SO_4^{-\cdot} + SO_4^{2-} \quad (4b)$$

where Tl(III) indicates all the thallium(III) ions of the aquated and hydroxo species. The k_4 is described as:

$$k_4 = \frac{k_{4a}[H^+] + k_{4b}K_{TlOH}}{[H^+] + K_{TlOH}} \quad (24)$$

where $K_{TlOH} = [TlOH^+][H^+]/[Tl^{2+}(aq)]$.

Since K_{TlOH} is 3×10^{-5} mol dm^{-3} at 25 °C, Eq. 25 will be satisfied at concentrations larger than 3×10^{-3} mol dm^{-3} of [H$^+$].

$$k_4 = k_{4a} + k_{4b}K_{TlOH}[H^+]^{-1} \quad (25)$$

The plot of k_4 *vs.* $[H^+]^{-1}$ showed a straight line, as in Fig. 4. The k_{4a} and k_{4b} were obtained as 250 and 9×10^5 dm^3 mol^{-1} s^{-1} from the intercept and the slope respectively. Thus, at a hydrogen-ion concentration of 0.01 mol dm^{-3}, 92% of k_4 corresponds to the second term of Eq. 25. The plot of k_4 *vs.* $[H^+]^{-1}$ greatly deviated from the linear line in the more alkaline region; thus, the $Tl(OH)_2$ species participated in the reaction.

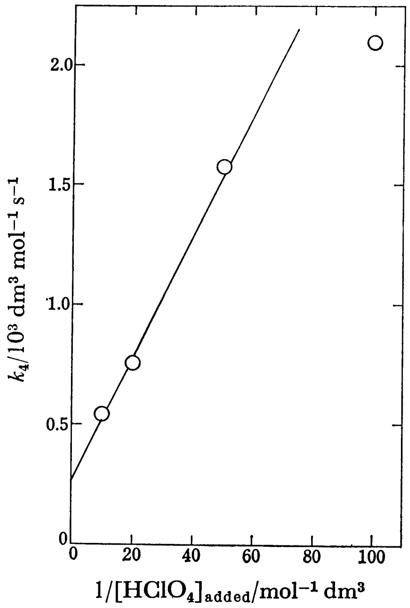

Fig. 4. Plot of k_4 *vs.* $1/[HClO_4]_{added}$ (Eq. 25). Conditions as in Table 4.

It should be noted here that the pH dependence of k_5 is so small as to be constant at hydrogen-ion concentrations over the range from 0.001 to 0.1 mol dm^{-3}. By the same treatments as used for the k_4 values, the following equations are obtained:

$$Tl^{2+}(aq) + Tl^{2+}(aq) \xrightarrow{k_{5a}} Tl(I) + Tl(III) \quad (5a)$$

$$Tl^{2+}(aq) + TlOH^+ \xrightarrow{k_{5b}} Tl(I) + Tl(III) \quad (5b)$$

$$k_5 = k_{5a} + k_{5b}K_{TlOH}[H^+]^{-1} \quad (26)$$

The k_5 at 25 °C is 3.0×10^9 dm^3 mol^{-1} s^{-1} at pH 5.6[13] and 5.2×10^8 dm^3 mol^{-1} s^{-1} at 0.1 mol dm^{-3} of [H$^+$].[14] Thus, Eq. 26 is written as Eq. 27:

$$k_5 = 5.2 \times 10^8 + 6.2 \times 10^3[H^+]^{-1} \quad (27)$$

Equation 27 indicates that the k_5 is actually constant at hydrogen-ion concentrations larger than 6×10^{-4} mol dm^{-3}. Falcinella *et al.*[14] have reported that the k_5 value was independent of the acid concentrations over the range from 0.1 to 1.0 mol dm^{-3} and was slightly dependent on the temperature with an activation free energy, ΔG_5^*, of 7.9 ± 1.5 kJ mol^{-1}. From the temperature dependences for k_1 and k_b shown in Tables 5 and 6, the activation energies,

E_1 and E_b, derived from an Arrhenius plot were 157 and 108 kJ mol^{-1} respectively. Thus, the value of E_4 is obtained as 33 kJ mol^{-1} by the relationship of $E_b=E_4+(E_1-E_5)/2$.

Although Reaction 1 is not sensitive to the ionic strength, the k_4 and k_5 values are probably dependent on the ionic strength, because Reactions 4 and 5 are reactions between two ions of unlike and like signs. Thus, the k_b value which is composed of $k_4(k_1/k_5)^{1/2}$ may be thought to be largely dependent on the ionic strength. However, the ionic-strength dependence on k_b was not very large: the slope value for the plot of log k_b *vs.* $\mu^{1/2}$ was -1.05, an almost equivalent to the case of the reaction between two univalent-ions of unlike signs expected for the equation of $\log k=\log k_0+1.02\ Z_-Z_+\ \mu^{1/2}$. As has been mentioned already, the k_{4b} term in Eq. 25 was calculated to be 92% of k_4 under the condition of a hydrogen-ion concentration of 0.01 mol dm^{-3}, this condition being the same as in the experiments for the ionic-strength dependence. Thus, the effective charges of the thallium(II) ion may be close to unity, smaller effective charges may cause the smaller dependence of the k_b on the ionic strength.

In a subsequent paper the reaction between thallium(I) and peroxodisulfate in alkaline solution will be discussed.

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