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Oxidative Reaction of Thiosulfate with Hydrogen Peroxide by Freezing

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In order to investigate the characteristics of the oxidative reactions of low-valence sulfur compounds with H_2O_2 in the freezing process, a $Na_2S_2O_3$ aqueous solution was mixed with a H_2O_2 aqueous solution, followed by freezing at -15 °C. After the designated time had passed, the concentrations of sulfur compounds were measured. The oxidation of thiosulfates was accelerated due to the freeze-concentration effect. The maximum reaction rate of the freezing reaction (-15 °C) was about 20-times faster than that in an aqueous solution (25 °C). In the aqueous-phase reaction, thiosulfates were transformed to tetrathionates as intermediates, or directly to sulfates, and all sulfur compounds were finally oxidized to sulfates. On the other hand, the tetrathionates and sulfates transformed by the freezing reaction were preserved in ice for a long time. The maximum amounts of the tetrathionates formed by freezing were about twice those in the aqueous-phase reaction. Once tetrathionates were formed by the freezing reaction, most of the formed tetrathionates coexisting with high concentrations of H_2O_2 were not transformed to sulfate, regardless of whether or not the sample was re-frozen. This observation is probably attributable to the difference in the pH value when tetrathionates are formed.

The oxidative reaction of various sulfur compounds with hydrogen peroxide in aqueous solution has been reported for many years. From the 1970s, the oxidative reaction of H_2S with H_2O_2 has been employed for the treatment of odors due to the generation of H_2S in sewage-treatment systems.[1] Extensive investigations of the kinetics and the reaction mechanism of this oxidative reaction were made by Hoffmann[1] and Ràbai et al.[2] Millero et al. reported on the oxidation of H_2S with H_2O_2 in high ionic-strength solutions, such as seawater and NaCl solution.[3] In the oxidation of H_2S with H_2O_2, polysulfides and sulfite are formed as the intermediates, and the polysulfides react with the sulfite to produce thiosulfate.[4]

Because the formation of thiosulfate is faster than the transformation of sulfite to sulfate, the oxidation of thiosulfate with H_2O_2 is the major pathway to produce sulfate as the final product. The oxidation of thiosulfate with H_2O_2 was extensively investigated by Yokosuka et al.[5] According to their study, polythionates are formed during the course of the oxidation of thiosulfate:

$$2S_2O_3{}^{2-} + H_2O_2 \rightarrow S_4O_6{}^{2-} + 2OH^-, \tag{1}$$

$$3S_2O_3{}^{2-} + 4H_2O_2 \rightarrow 2S_3O_6{}^{2-} + 2OH^- + 3H_2O. \tag{2}$$

Reactions (1) and (2) take place at any pH regions, while the reactions (3)–(5) proceed so slowly at pH 4 that the final products are only tri- and tetrathionates following:

$$S_2O_3{}^{2-} + 4H_2O_2 \rightarrow 2SO_4{}^{2-} + 2H^+ + 3H_2O, \tag{3}$$

$$S_4O_6{}^{2-} + 7H_2O_2 \rightarrow 4SO_4{}^{2-} + 6H^+ + 4H_2O, \tag{4}$$

$$S_3O_6{}^{2-} + 4H_2O_2 \rightarrow 3SO_4{}^{2-} + 4H^+ + 2H_2O. \tag{5}$$

At higher pH regions, tri- and tetrathionates are oxidized to form sulfate besides the direct oxidation of thiosulfate to sulfate.

Freezing has been widely used as a preservation method in the fields of food chemistry and biochemistry. On the other hand, some reactions are known to be accelerated by freezing in the same fields.[6–14] Fennema summarized several suggested mechanisms for the acceleration, and reported that the freeze-concentration effect was considered to be the most important mechanism.[14] Our previous study also suggests that the acceleration of the rate of the oxidation reaction from nitrite to nitrate by freezing is induced by the rapid confinement of reactants in grain boundaries between ice crystals.[15] Because freezing is an ordinary process in the environment that contributes significantly to various precipitation processes,[16] the accelerated reaction induced by freezing may have a certain amount of impact on the atmosphere. We previously showed the implication that the oxidative reaction of nitrite with dissolved oxygen accelerated by the freezing process plays an important role in the nitrite sink process in the tropospheric aqueous phase.[17]

Because H_2O_2 is a dominant oxidant in clouds, fogs, or rain in the atmosphere, the oxidations of S(IV) or sulfur compounds having lower oxidation states with H_2O_2 are considered to be the most significant chemical transformations in cloudwater.[18] The reaction of S(IV) with H_2O_2 and its atmospheric impactions have been studied by several research groups.[19–21] Considering the importance of the freezing process and the oxidative reactions of sulfur species with H_2O_2 in the environment, the elucidation of the chemical transformations of sulfur compounds with H_2O_2 in the freezing process will contribute toward our understanding of the sulfur cycle in the environment. Moreover, this study can be applied to odor treatments, such as the reactions of foul-smelling substances with H_2O_2. In our previous study, a rapid reaction of sulfide with H_2O_2 by freezing was reported.[22] The maximum reaction rate in freezing was about 5-times faster than that in solution. Thiosulfate, sulfite, and the unknown sulfur compound were detected as intermediates in the reaction by freezing. All sulfides, thiosulfates, and sulfites were consumed when a solution was completely frozen, while an unknown sulfur compound was not further transformed and preserved in ice. On the other hand, all sulfur compounds were eventually transformed to sulfate in an aqueous solution. We assumed that this unknown sulfur compound was tetrathionate. In this work, comparisons of the reaction rates and the final products in the freezing process and in an aqueous solution were demonstrated when thiosulfate reacted with H_2O_2. Based on these comparisons, the characteristics of the oxidative reaction of thiosulfate by freezing are discussed. Furthermore, the unknown sulfur compound in our previous study was determined, and the difference in the reactivity of the unknown sulfur compound between in ice and in an aqueous solution is reported.

Experimental

All regent-grade chemicals, except for $K_2S_3O_6$, were obtained from Wako Pure Chemicals, Inc., and used without further purification. $K_2S_3O_6$ is a labile compound, and is not commercially available. Therefore, $K_2S_3O_6$ was synthesized according to a previously reported procedure.[23] Pure water was prepared by using a Simpli Lab-UV ultrapure water system (Nihon Millipore, Ltd.) after deionized water was distilled. The resistivity of pure water exceeds 18.2 MΩ cm.

Sulfide and sulfite are known to be oxidized by dissolved oxygen.[22,24,25] Some thiosulfate may also be oxidized by dissolved oxygen, but we confirmed that the composition of 100.0 µmol dm^{-3} of $Na_2S_2O_3$ aqueous solution was not changed throughout the experimental period when the solution was left at room temperature. Therefore, dissolved oxygen in pure water was not purged with an inert gas in this experiment. The pH of the solution was not adjusted, and it was measured to be about 6 for 50.0 µmol dm^{-3} of $Na_2S_2O_3$ and 1.00 mmol dm^{-3} of H_2O_2 aqueous solution.

The experimental procedure is described as follows. Equal volumes (5 cm^3) of a $Na_2S_2O_3$ aqueous solution and a H_2O_2 aqueous solution were mixed well. The typical concentrations of $Na_2S_2O_3$ and H_2O_2 before mixing were 100.0 µmol dm^{-3} and 2.00 mmol dm^{-3}, respectively. Immediately after mixing, an aliquot of the mixture samples was put into a sealed polypropylene syringe with a septum, and the syringe was immersed in a thermostat at −15 °C. This point of time was defined as the initial condition. After a designated time, the frozen sample was thawed in a hot-water bath, and the concentrations of ions in the thawed sample were measured. In this way, time profiles of each ion concentration were obtained by a set of different experimental runs in the freezing experiments. Other samples were kept in a polypropylene vessel at 25 °C for control experiments. In the control experiments, an aliquot of the sample solution was analyzed at designated intervals.

Sulfide was determined by the methylene-blue method.[26] The concentrations of sulfite and sulfate were determined using a Metrohm, Ltd. 761 Compact IC ion chromatographic analyzer with an SI-90 column from the Showa Denko Co., Ltd. (eluent solution: 1 mmol dm^{-3} $NaHCO_3$ and 3 mmol dm^{-3} Na_2CO_3; flow rate: 1.2 cm^3 min^{-1}). The concentrations of thiosulfate, trithionate, and tetrathionate were determined according to Zou et al.[27] using a PU 610 HPLC pump and a UV 620 UV-visible detector, both of which were obtained from the GL Science, Inc. The flow rate in the HPLC system was 0.4 cm^3 min^{-1}, and the absorption wavelength of the detector was set at 218 nm. The column used in the HPLC system was a GL Science, Inc., Inertsil ODS-3 (2.1 mm i.d. × 150 mm length), and the eluent solution was a 3 mM $(C_4H_9)_4NOH$ and 2 mM Na_2CO_3 mixture in (26 + 74) $CH_3CN + H_2O$. The concentration of H_2O_2 was determined by an iodometric method.[28] The pH of the sample was measured with a pH meter (the Horiba, Ltd., M-13 desktop pH meter and the Horiba, Ltd., 6069-10C glass electrode), which was calibrated with pH 4, 7, and 9 buffer solutions.

Results and Discussion

1. Reaction of Thiosulfate with Hydrogen Peroxide in an Aqueous Solution. First of all, the reaction in an aqueous solution was investigated in order to compare the reaction rate in a freezing process and that in an aqueous solution. Figure 1 shows the time profile of the reaction of thiosulfate with H_2O_2 in an aqueous solution. As the reaction proceeded, thiosulfates were transformed to tetrathionates (reaction (1)) or directly to sulfates (reaction (3)). The formation of trithionates, expressed by the reaction (2), was reported to be observed during the course of the reaction of the thiosulfates with H_2O_2.[5] However, trithionate was not detected throughout this experiment. The reason is probably that the concentration of thiosulfate is not sufficient to produce trithionates. As observed in the reaction of sulfide with H_2O_2,[22] all thiosulfates were finally transformed to sulfates, based on the results of Fig. 1.

Figure 1 also gives a summation of the detected sulfur compounds. The unknown sulfur compounds were formed at the beginning of the reaction. In our previous study of the oxidative reaction of sulfite and dissolved oxygen in an aqueous solution, $S_2O_5^{2-}$ or $S_2O_7^{2-}$ was assumed to be

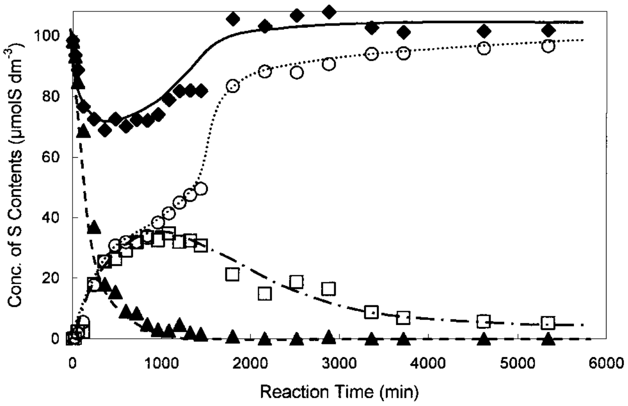

Fig. 1. Time profile of the reaction of thiosulfate with hydrogen peroxide at 25 °C and pH 6. $[Na_2S_2O_3]_0$: 50.0 µmol dm^{-3}, $[H_2O_2]_0$: 1000.0 µmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}, ◆: Summation of the detected sulfur compounds.

formed as an intermediate.[25] Because the transformation of $S_2O_5^{2-}$ or $S_2O_7^{2-}$ to sulfates was very slow, these intermediates would accumulate during the course of the oxidation of sulfur compounds. At the beginning of this experiment, a trace amount of sulfite was detected. This observation suggests that the formed sulfite was immediately transformed to $S_2O_5^{2-}$ or $S_2O_7^{2-}$, and $S_2O_5^{2-}$ or $S_2O_7^{2-}$ was transformed to sulfate very slowly. $S_2O_5^{2-}$ and $S_2O_7^{2-}$ could not be determined by using our analytical system.

The summation at the final stage was well balanced by that in the initial condition. Therefore, we quantitatively confirmed that most of the unknown sulfur compounds observed in the reaction of sulfide with H_2O_2[25] were tetrathionates. The reaction rate in the aqueous solution was very slow. It took about 900 minutes to consume all thiosulfates and more than 5,000 minutes to consume all tetrathionates.

2. Reaction of Thiosulfate with Hydrogen Peroxide by Freezing. Figure 2 shows the time profile of the reactions of thiosulfate with H_2O_2 when the sample solution was frozen. The whole sample was seemingly frozen for 12 minutes, but some thiosulfates remained in ice at that time. The remaining thiosulfates were presumed to react in the grain boundaries of ice crystals. Most thiosulfates were consumed within 60 minutes. The reaction rate was much faster than that in the aqueous solution at 25 °C. The maximum reaction rate of the reaction by freezing was about 20-times faster than that in the aqueous solution. This increase in the reaction rate is supposed to be due to the freeze-concentration effect, which is discussed in our previous paper.[15] As is the case with the reaction in the aqueous solution, tetrathionates and sulfates were formed in the course of the reaction by freezing. However, the maximum yield of tetrathionates in the freezing reaction was about twice that in the aqueous reaction. Another distinctive difference between the freezing reaction and the reaction in aqueous solution is that the formed tetrathionates were not further transformed. The composition of the sample was not altered after 60 minutes within this observation period. This result suggests that reaction (1) proceeds rapidly because of the freeze-concentration effect, while reaction (4) hardly proceeds in ice.

The summation of the sulfur contents at the final stage was about 91% of the total sulfur contents in the initial condition. This difference could be attributable to the formation of $S_2O_5^{2-}$ or $S_2O_7^{2-}$. As mentioned above, the transformation of $S_2O_5^{2-}$ or $S_2O_7^{2-}$ is very slow. The formed $S_2O_5^{2-}$ or $S_2O_7^{2-}$ would be stable in the grain boundaries of ice crystals.

3. Effect of the Concentration of Hydrogen Peroxide on the Oxidation of Thiosulfate. In the freezing reaction, not all of the sulfur compounds were transformed to sulfates. Grant and Alburn reported that H_2O_2 in ice degraded rapidly with the existence of Fe(III) or Cu(II).[11] Therefore, H_2O_2 may degrade by freezing, and can not attain a sufficient concentration to oxidize all of the sulfur compounds to sulfates. In the experiments mentioned above, the concentration of H_2O_2 was also measured. During the oxidation of thiosulfates in both an aqueous solution and a freezing reaction, H_2O_2 continued to be excessive (more than 600.0 μmol dm^{-3}) in the sample. We confirmed that freezing did not degrade H_2O_2. In order to investigate the effect of the concentration of H_2O_2 on the reaction system of thiosulfate with H_2O_2, the initial concentrations of H_2O_2 were varied, and the final products in the freezing reaction were measured. The freezing time was 4 hours in all of the experimental runs, and, thus, the oxidative reaction was not assumed to proceed further. Figure 3 shows the results. Only tetrathionates and sulfates were finally produced in all cases. Under the condition that the initial concentration of H_2O_2 exceeds 500.0 μmol dm^{-3}, the composition of the frozen sample remains constant. It is clear that an excessive concentration of H_2O_2 does not affect the yields of tetrathionates and sulfates. The same observation was obtained in the freezing reaction of sulfide with H_2O_2.[22]

4. Reactivity of the Formed Tetrathionate with Hydrogen Peroxide in the Freezing Reaction and in the Aqueous Phase Reaction. As shown in Figs. 1 and 2, the tetrathionate formed by freezing was stable in ice over a long period of time, while that formed in an aqueous solution was transformed to sulfate. These were interesting phenomena. Then, the reactivity of the tetrathionate formed by the freezing reaction was investigated. Immediately after preparing 50.0 μmol dm^{-3} of thiosulfate and 1.00 mmol dm^{-3} of a H_2O_2 mix-

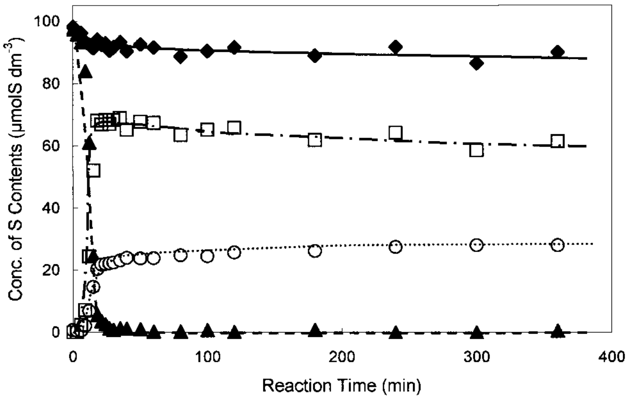

Fig. 2. Time profile of the reaction of thiosulfate with hydrogen peroxide by freezing at −15 °C and pH 6. [$Na_2S_2O_3$]$_0$: 50.0 μmol dm^{-3}, [H_2O_2]$_0$: 1000.0 μmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}, ◆: Summation of the detected sulfur compounds.

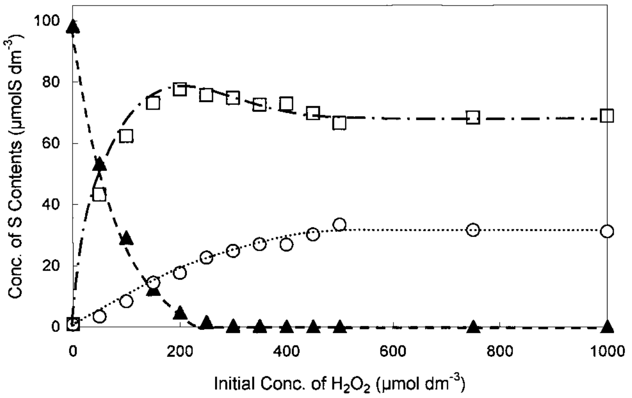

Fig. 3. Final products of the reaction of thiosulfate with the various initial concentrations of hydrogen peroxide at −15 °C and pH 6. [$Na_2S_2O_3$]$_0$: 50.0 μmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}. The freezing reaction time was 4 hours.

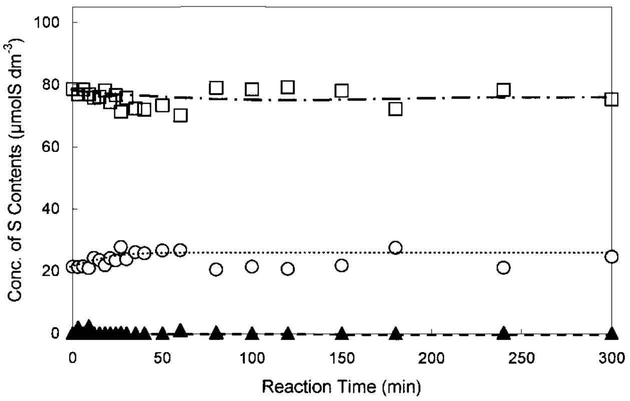

Fig. 4. Time profile of the reaction of the formed tetrathionate with hydrogen peroxide by re-freezing at −15 °C and pH 6. $[Na_2S_2O_3]_0$: 50.0 μmol dm^{-3}, $[H_2O_2]_0$: 1000.0 μmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}. The initial condition was defined as the moment when the sample was frozen again.

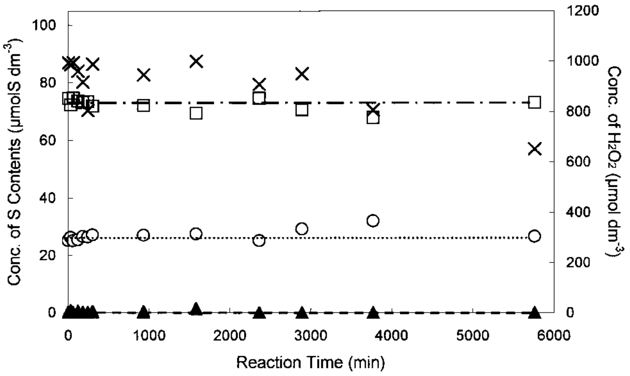

Fig. 5. Time profile of the reaction of the formed tetrathionate with hydrogen peroxide at 25 °C and pH 6. $[Na_2S_2O_3]_0$: 50.0 μmol dm^{-3}, $[H_2O_2]_0$: 1000.0 μmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}, ×: H_2O_2. The initial condition was defined as the moment when the sample was thawed after the first freezing.

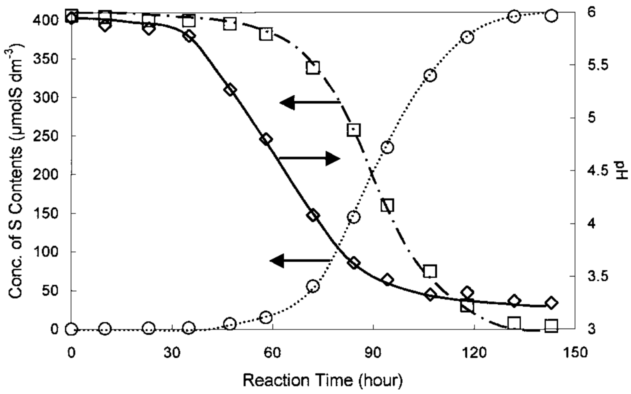

Fig. 6. Time profile of the reaction of the tetrathionate with hydrogen peroxide at 25 °C. $[Na_2S_2O_3]_0$: 50.0 μmol dm^{-3}, $[H_2O_2]_0$: 1000.0 μmol dm^{-3}. □: $S_4O_6^{2-}$, ○: SO_4^{2-}, ◇: H_2O_2. The initial pH of the sample was 6.0.

ture solution, the sample was frozen for 110 minutes. Figure 2 shows that about 17.0 μmol dm^{-3} of tetrathionate (68.0 μmol dm^{-3} in the concentration of sulfur compound) and about 25.0 μmol dm^{-3} of sulfate were produced during that freezing period. After the freezing reaction, the sample was thawed in a hot-water bath. Some samples containing tetrathionates and sulfates were re-frozen and left in a thermostat at −15 °C. Other samples were kept at 25 °C for control experiments. After the second reaction by freezing, or in an aqueous solution, the compositions of the samples were measured. Figure 4 shows the results of the freezing reaction. Most of the formed tetrathionates were not transformed during the course of freezing, or in the grain boundaries. Consequently, tetrathionates may be preserved in ice. Figure 5 shows the results of the aqueous phase reaction. Even in this case, the formed tetrathionates were not transformed to sulfates. In addition, a large excess of H_2O_2 remained. This result is inconsistent with that shown in Fig. 1, in which all tetrathionates were oxidized to sulfates in an aqueous solution.

In summary, once the sample was frozen, tetrathionates were produced at a rate twice that in an aqueous solution. Whether or not the sample was re-frozen, most of the formed tetrathionates were not transformed to sulfate.

5. The pH Dependence of the Reactivity of Tetrathionate with Hydrogen Peroxide. The reason why tetrathionates are not oxidized by H_2O_2 after the freezing process is probably attributable to the difference in the pH value when tetrathionates are formed during the course of the reaction of thiosulfates with H_2O_2. In the aqueous-phase reaction, the pH of the sample was changed from 4.98 at 1080 minutes (when the maximum amount of tetrathionates was formed) to 4.76 at 5340 minutes (Fig. 1). On the other hand, the pH of the sample was changed from 6.35 at 40 minutes (when the maximum amount of tetrathionates was formed) to 6.08 at 360 minutes in the freezing reaction (Fig. 2). Accordingly, we investigated the rate of the oxidation of tetrathionates with H_2O_2 at the initial pH 6.0. Equal volumes of a $Na_2S_4O_6$ aqueous solution and a H_2O_2 aqueous solution were mixed well, and samples were kept in a polypropylene vessel at 25 °C or at 1 °C. The time profiles of concentrations of sulfur compounds were measured. Figure 6 shows that the oxidation rate of tetrathionates increased with decreasing the pH values. The oxidation rates, $-d[S_4O_6^{2-}]/dt$, at pH 6.0 and pH 5.0, were obtained to be −0.14 μmol S dm^{-3} h^{-1} and −1.45 μmol S dm^{-3} h^{-1}, respectively. The oxidation rate at pH 5.0 is almost the same as the maximum decrease rate of tetrathionates in the experiment shown in Fig. 1 (−1.35 μmol S dm^{-3} h^{-1}). The decrease in the oxidation rate at a lower pH region was probably due to a shortage of tetrathionates. From the obtained data, it was concluded that the lower pH of the sample solution brought about a faster oxidation of tetrathionates.

Under the conditions of 1 °C and pH 4.0–6.0, the oxidation of tetrathionates was not promoted for over 9000 minutes. This oxidative reaction would be suppressed at low temperatures. The temperature of the grain boundaries of ice crystals is expected to be the same as that in the thermostated condition (−15 °C). Consequently, once tetrathionates were formed in the freezing process, they were not trans-

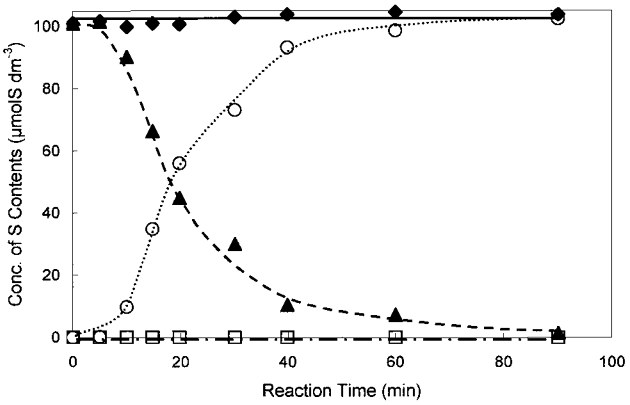

Fig. 7. Time profile of the reaction of thiosulfate with hydrogen peroxide by freezing at −15 °C and pH 10. [$Na_2S_2O_3$]$_0$: 50.0 μmol dm^{-3}, [H_2O_2]$_0$: 1000.0 μmol dm^{-3}. ▲: $S_2O_3^{2-}$, □: $S_4O_6^{2-}$, ○: SO_4^{2-}, ◆: Summation of the detected sulfur compounds. The pH of the sample was adjusted by using a NaOH solution.

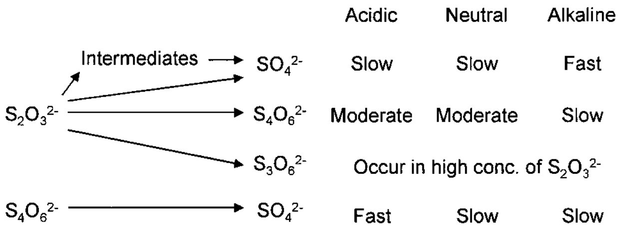

Fig. 8. The summary of the reaction paths of the oxidative reaction of thiosulfate with hydrogen peroxide by freezing.

formed further, and were preserved in the grain boundaries of ice crystals.

The observation in the experiment shown in Fig. 6 seems to be inconsistent with that obtained by Yokosuka et al.[5] Yokosuka et al. found that reactions (3)–(5) proceeded very slowly in the lower pH region (pH 4), and, thus, the final products were only tri- and tetrathionates. At higher pHs, the oxidation of tri- and tetrathionates to form sulfate took place in addition to the direct oxidation of thiosulfate to sulfate (reaction (2)). The difference between our study and theirs is attributed to the experimental conditions. First, the initial concentrations of thiosulfates and H_2O_2 in the former study were 10-times and 20–100-times higher than those in our study, respectively. Second, the reaction time in the investigation made by Yokosuka et al. (up to 3 hours) was much shorter than that in our study (over 100 hours). Yokosuka et al. do not seem to confirm whether or not the tetrathionates formed under the neutral or acidic condition will degrade in a long-term observation. We also investigated the reaction of thiosulfate and H_2O_2 in the alkaline condition. Figure 7 shows the results. At the initial pH 10, no formation of tri- and tetrathionates was observed, and all sulfur compounds were transformed to sulfates. The oxidative reactions to form sulfates (reactions (3)–(5)) were assumed to occur so fast that no intermediates could be observed under the alkaline conditions.

The reaction paths of the oxidative reaction of thiosulfate by freezing are summarized in Fig. 8. The oxidation of thiosulfates is exceedingly fast under alkaline conditions. Under neutral or acidic conditions, the oxidation rate of tetrathionates increases with decreasing the initial pH value in a long-term observation. The reactivities of most sulfur compounds with H_2O_2 largely depend on the pH value.[1–5] This study shows that the freezing reaction regulates the pH of the sample, and that this characteristic controls the reaction rate and the yields of the final products.

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