On the Exchange of Sulphur between Dithionite and Thiosulphate and between Tetrathionate and Sulphate Ions

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The exchange of sulphur atoms between dithionite and thiosulphate ions as well as between tetrathionate and sulphate ions has been investigated at room temperature by a tracer method using ^{35}S as a radioactive indicator.

The former system was investigated in two different solutions, an alkaline ($\text{pH} \sim 13$), and a slightly acid one ($\text{pH} \sim 6$), the time of exchange being varied with an upper limit of 44 h in the alkaline solution and 1.25 h in the weakly acid one. No exchange of sulphur atoms could be detected.

The system tetrathionate-sulphate was studied in neutral to weakly acid solutions with a maximum time of exchange of 44 h. No exchange of sulphur atoms could be detected.

In a previous paper¹ it has been reported that the exchange of sulphur atoms between dithionite and thiosulphate as well as between tetrathionate and sulphate ions was being studied. The present paper gives a full report of the experimental procedure and the results of the investigation.

EXPERIMENTAL

Syntheses. The isotopic exchange reactions were performed using ^{35}S as labelled atoms. The ^{35}S preparations were supplied by A.E.R.E., Harwell, Berkshire, England.

The following active ions were prepared: $\text{S}^*\text{SO}_3^{2-}$, $\text{SS}^*\text{O}_3^{2-}$, $\text{O}_3\text{SS}^*\text{SSO}_3^{2-}$, $\text{O}_3\text{S}^*\text{SSSO}_3^{2-}$, and $\text{S}^*\text{O}_4^{2-}$; S^* representing the radioactive isotope ^{35}S . The two different radioactive thiosulphate ions were prepared according to conventional methods², *i. e.* boiling an alkaline sulphite solution together with solid sulphur, one of the reactants being labelled with ^{35}S . The following reactions take place:

* The author, unfortunately, died suddenly before completing this investigation. This paper presenting the results obtained by him, has been written by Mr. B. Mueller.

After the boiling, the solutions were filtered in order to separate any solid sulphur that might remain. It was checked that the solutions did not contain any unreacted sulphite ion. To a small part of the solution was added a strontium solution. If no precipitate appeared all sulphite ion had been used up in reactions (1) and (2).

The radioactive sulphite solution used for reaction (2) was produced by combusting radioactive sulphur in a stream of air which was sucked into a wash bottle containing a dilute sodium hydroxide solution.

The two tetrathionate ions mentioned above were prepared according to reactions (3) and (4).

These preparations were made partly according to a method described by Sander³ and modified by Martin and Metz⁴ resulting in a solid product, and partly by pouring active thiosulphate solution into an excess of iodine solution. When using the latter method the preparations were made immediately before starting an exchange experiment.

The radioactive sulphate ions were made by oxidation of sulphur dioxide in a 5 % hydrogen peroxide solution.

The commercially available preparations of sodium dithionite are highly contaminated by decomposition products, *e.g.* sulphite, thiosulphate, sulphate. These preparations had thus to be purified. From their solution in dilute sodium hydroxide, the unstable hydrate $Na_2S_2O_4 \cdot 2H_2O$ was precipitated by addition of solid sodium hydroxide. On heating to about 60° C, the hydrate lost its water of hydration. The product thus formed was freed from the mother-liquid by washing with absolute alcohol and finally dissolved in about 0.1 *M* sodium hydroxide solution, this solution being stored in a stoppered bottle in a nitrogen atmosphere.

Other chemicals used were of analytical reagent grade quality.

Analyses. The analyses of sodium dithionite were performed according to Zocher and Saechtling⁵. The metallic silver was separated and determined by Volhard titration.

The tetrathionate preparations are analyzed according to a method given by Kurt-nacker⁶. The solid preparations contained 99 % sodium tetrathionate and about 1 % thiosulphate.

PROCEDURE USED IN EXCHANGE EXPERIMENTS

1. The system $S_2O_4^{2-} - S_2O_3^{2-}$. The isotopic exchange reactions were performed at room temperature — some in an alkaline solution (0.1 *M* NaOH, pH ~ 13) and some in a slightly acid solution (acetate buffer, pH ~ 6). In the alkaline medium, a radioactive thiosulphate solution was mixed with an inactive sodium dithionite solution, the total concentrations of the two ions being both 0.015 *M*. The mixture was stored in a closed glass bottle in a nitrogen atmosphere to avoid unnecessary oxidation. The exchange was interrupted by oxidizing the solution with iodine. If the oxidation is carried out in a slightly acid solution the following well known reactions take place:

To obtain an oxidation at the right acidity, an iodine-iodide solution containing an acetate buffer (pH = 5) was prepared. The exchange solution was poured into an excess of this solution. The sulphate ions produced according to reaction (5) were precipitated by the addition of an excess of barium ions. The barium sulphate precipitate, No. 1, was separated from the mother liquor by centrifugation. The tetrathionate ions formed according to (6) were oxidized by boiling the remaining solution with bromine-water. The sulphate ions now formed were precipitated as barium sulphate, No. 2. The sulphur atoms in ppt. No. 1 thus originated exclusively in the dithionite ions while ppt. No. 2 only contained sulphur atoms which existed in the thiosulphate ions at the end of the exchange.

In the acid solution the procedure was slightly altered. Owing to the rather rapid decomposition of dithionite in such a medium the pH of the solutions containing dithio-

nite were lowered to *ca.* 6 immediately before starting the exchange experiments. In these solutions the dithionite ions decompose giving thiosulphate, hydrogen sulphite, sulphate and sulphur. According to Van Der Heijde ⁷ there is an instantaneous and complete exchange of sulphur atoms between dithionite and hydrogen sulphite ions in neutral and acid solutions. He could not detect any exchange in alkaline solutions. In order to avoid errors caused by an exchange of sulphur atoms with hydrogen sulphite this component was separated from the dithionite solutions by adding an excess of strontium ions. All of the strontium sulphite precipitate was removed by filtration before adding the radioactive thiosulphate solution and starting the exchange. As the dithionite decomposes continually, fresh precipitate is formed in the exchange solution all the time. To avoid mixing this precipitate with the strontium sulphate formed by the oxidation of dithionite ions with iodine at the end of the exchange, the exchange solution was made to pass through a filter paper directly into the iodine-iodide solution. The strontium sulphate thus formed (ppt. No. 1) contained only the sulphur atoms from the dithionite ions still present at the end of the exchange. The mother liquor was treated in the same way as described above, the only difference being that ppt. No. 2 as well as No. 1 consisted of strontium sulphate instead of barium sulphate.

Due to the greater rate of decomposition of dithionite ions in the slightly acid solution than in the alkaline one, the time of exchange had to be shortened, the time used being 75 minutes instead of up to 44 hours in the latter medium.

2. The system $S_4O_6^{2-} - SO_4^{2-}$. These exchange experiments were made at room temperature in a neutral medium. In such a solution the tetrathionate ions disintegrate, partly forming sulphate ions ⁸. It is therefore necessary to remove the sulphate ions so formed before mixing the radioactive tetrathionate solution with the inactive sulphate solution. This is done by the addition of a known amount of barium ions. All sulphate ions as well as the thiosulphate ions that might be present are thus precipitated. Finally inactive sulphate ions are added in such a quantity that the concentration ratio, tetrathionate:sulphate, will be about 1:2 in the solution. The precipitates were separated from the mixture by filtering. The time of exchange in these experiments varied between 10 min. and 44 h. The exchange was interrupted by addition of a surplus of barium ions. The precipitated sulphate was separated from the mother liquor by centrifugation. The tetrathionate ions in the mother liquor were oxidized to sulphate ions and precipitated as barium sulphate by the same method as previously described. These two precipitates were recovered for subsequent activity measurements.

To check the results obtained, one experiment was carried out using radioactive sulphate ions and inactive tetrathionate ions.

Sample preparation and Counting Techniques. The sulphate precipitates, the radioactivity of which had to be determined were prepared according to Hevesy ⁹. In order to avoid the necessity of correcting the measured activities for selfabsorption all samples were of "infinite thickness". The measured activities of different samples are hereby directly comparable. All activity measurements were performed over a period of at least five minutes, using a bell-jar counter with a very thin window connected to a "SC 33 1000 Scaler" from Tracerlab. Inc., Boston, Mass., U. S.

RESULTS

1. The system $S_2O_4^{2-} - S_2O_3^{2-}$

Owing to the inequality of the sulphur atoms in thiosulphate ¹⁰, separate isotopic exchange experiments were carried out with the two different thiosulphate ions synthesized as described above. Table 1 presents some detailed experimental results.

All activity values in Table 1 as well as in Table 2 are the measured activities minus the natural background activity.

Table 1.

Expt. No.	Active ions used	Time of exchange min	pH	Counts per min for ppt. No. ^a			Fraction of original activity for ppt. No. ^a	
				1	2	3	1	2
1	S*SO ₃ ²⁻	2 640	13	109	3 829	4 061	0.03	0.95
2	SS*O ₃ ²⁻	0.67	13	263	5 977	5 787	0.05	1.03
3	—»—	286	13	286	5 564	5 787	0.05	0.96
4	—»—	1 380	13	256	5 657	5 787	0.04	0.98
5	S*SO ₃ ²⁻	75	6	3	3 529	4 256	0.00	0.83

The results indicate that under the prevailing circumstances no exchange of sulphur atoms between dithionite and thiosulphate ions occurs. The rather small activities recorded for ppt. No. 1 are presumably, at least, partly due to the decomposition of the tetrathionate ion formed by the iodine oxidation, the tetrathionate ions being far from stable in the slightly acid solution ⁸. The fact that the measured activities of ppt. No. 1 in experiments Nos 2, 3, and 4 are practically constant although the time of exchange is varied from 40 sec. to 23 h is definite evidence for the absence of a measurable exchange of sulphur atoms between dithionite ions and the central sulphur atom in thiosulphate ions within 23 h. If a slow exchange had occurred the recorded activities for ppt. No. 1 should have changed with time according to a reaction of the first order ¹¹. In expt. No. 1 the activity of ppt. No. 1 is smaller than in expt. No. 4 although the time of exchange is almost doubled. This indicates that not even the outer sulphur atom in the thiosulphate ion takes part in any exchange with the sulphur atoms of dithionite ion.

The fact that for expt. No. 5 the sum of the activities of the ppts. Nos. 1 and 2 are definitely smaller than for ppt. No. 3, may be explained thus: Certain decomposition products of the dithionite ions, for instance S₂O₃²⁻, are during the separation precipitated together with the initially-labelled thiosulphate, resulting in a reduction of the registered activity. For the other experiments these differences are within the limits of experimental error.

2. The system S₄O₆²⁻—SO₄²⁻

In these experiments the two radioactive tetrathionate ions formed according to reactions (3) and (4) were used in different experiments. Table 2 gives some results.

From the results tabulated below it is evident that the variations with time of the activities of ppt. No. 1 for expts. Nos. 1, 2 and 3 do not follow a reaction of the first order. This is evidence for the absence of a measurable rate of exchange of sulphur atoms between O₃SS*SSO₃²⁻ and SO₄²⁻ within 43 h¹¹. For the other tetrathionate ion no variation of the time of exchange has

^a Ppt. No. 1 contains the sulphur atoms of the previously inactive dithionite ions.

Ppt. No. 2 contains the sulphur atoms of the previously active thiosulphate ions.

Ppt. No. 3 contains the sulphur atoms of the originally radioactive thiosulphate directly oxidized to sulphate and precipitated as barium sulphate.

Table 2.

Expt. No.	Active ions used	Time of exchange min.	Exchange solution	Counts per min. for ppt. No. ^a			Fraction of original activity for ppt. No. ^a	
				1	2	3	1	2
1	O ₃ SS*SSO ₃ ²⁻	10	Water	96	1 743	1 757	0.05	1.00
2	—»—	1 620	—»—	80	1 641	1 607	0.05	1.02
3	—»—	2 580	—»—	306	3 829	4 061	0.08	0.94
4	O ₃ S*SSSO ₃ ²⁻	2 640	Acetate buffer pH=6.2	72	5 874	5 890	0.01	1.00
5	S*O ₄ ²⁻	5	Water	45	1 783	2 611	0.02	0.68

been made. As the activity of ppt. No. 1 is smaller in expt. No. 4 than in expts. Nos. 1, 2 and 3 it is evident that no exchange occurred in this case either, within 44 h.

The considerable loss of activity of the originally-radioactive sulphate ions in expt. No. 5. after the exchange is due to the fact that a certain amount of the tetrathionate had formed sulphate ions by decomposition. In this experiment no separation of sulphate ions in the tetrathionate solution was performed before adding the radioactive sulphate ions to the solution.

DISCUSSION

As no exchange of sulphur atoms between dithionite and thiosulphate ions was found, it is not possible to conclude anything about the structure of the dithionite ions as regards equality or inequality of the chemical bonds between the sulphur atoms and the remaining part of the ion.

Regarding the system tetrathionate-sulphate the results prove once again the great stability of the bonds of the sulphur atom in the sulphate ion. No information about the chemical bonds in the tetrathionate ion, including the possible inequality of the chemical bonds of the different sulphur atoms as anticipated above, is given by the results obtained. Cf. a recent determination of the crystal structure of a tetrathionate compound ¹².

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^a Ppt. No. 1 contains the sulphur atoms of the originally inactive ions.

Ppt. No. 2 contains the sulphur atoms of the originally radioactive ions having been separated from the exchange solution.

Ppt. No. 3 contains the originally radioactive sulphur atoms directly oxidized to sulphate and precipitated as barium sulphate for activity measurements.

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Received July 1, 1954.