SULPHUR ISOTOPE CHEMISTRY OF POLYSULPHIDE SOLUTION

KINETIC ISOTOPE EFFECT IN THE THIOCYANIDIZATION

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Abstract—The kinetic isotope effect in S—S bond rupture in the reaction, $S_n'' + (n-1)CN' = S'' + (n-1)SCN'$, was estimated to be 1.022 at 24.8°C, the lighter isotope, ³³S, leaving the polysulphide chain faster than the heavy one, ³⁴S. The enrichment of the heavy isotope in the polysulphide and sulphide ions during the fractional removal of the polysulphidic sulphur was discussed in terms of the kinetic isotope effect and the isotope equilibrium between the polysulphide and sulphide ions.

It is apparent from the present result that the rate determining process of the reaction should involve the rupture of S—S bond.

THE ISOTOPIC properties of polysulphide solutions have been studied by several authors. KOROS *et al.*⁽¹⁾ found that the isotopic exchange of radiosulphur in polysulphide solutions takes place very rapidly through all species present in the solutions and all sulphur atoms in the bulk system can be considered isotopically equivalent. Individual species in the system, however, would be of slightly different isotopic properties from each other, the difference between sulphide and polysulphide ions being much greater than that between polysulphide ions of different chain length. The S—S bond in the latter will be strong enough to cause some enrichment of the heavy sulphur isotopes in them as compared with sulphide (and hydrosulphide) ion.

The S—S single bond, on the other hand, is easily broken by some reductants such as cyanide ion to form sulphide and thio-compounds. In a lower pH region, the chain quickly disproportionates into sulphide and elemental sulphur. In these reactions, the kinetic isotope effect of sulphur would be observed if the bond rupture is involved as a rate controlling step of the reaction. When this is the case, the lighter isotope is expected to leave the chain faster than the heavy one resulting in the enrichment of the latter in the polysulphide ions left unreacted. The isotopic ratio of the sulphide ion should also be varied by addition of the sulphide newly formed during the reaction as well as through the rapid isotopic exchange with polysulphide ions. Consequently, the observed isotope effect should be considered as a sum of the real kinetic isotope effect and the isotopic interaction between sulphide and polysulphide ions.

In the present research, we have studied the *apparent* kinetic isotope effect in the reaction, $S_n'' + (n-1)CN' \rightarrow S'' + (n-1)SCN'$, by means of sulphur of natural isotope abundance and a mass spectrometer for the precision isotope ratio measurement. From the results obtained, the kinetic isotope effect which may be defined in a rough sense as the inter-molecular isotope effect is estimated.

⁽¹⁾ E. KOROS, L. MAROS, I. FEHÉR and E. SCHULEK, *Magy. kém. Foly.* **63**, 213 (1957); *Chem. Abs.* **52**, 10789 (1958).

Terms

$$\begin{aligned} & Total \ sulphur: \sum_{n=1}^{\infty} \{n[\mathbf{S}_n''] + n[\mathbf{HS}_n'] + n[\mathbf{H}_2\mathbf{S}_n]\} \\ & Monosulphide \ sulphur: \sum_{n=1}^{\infty} \{[\mathbf{S}_n''] + [\mathbf{HS}_n'] + [\mathbf{H}_2\mathbf{S}_n]\} \end{aligned}$$

Polysulphide sulphur: the difference between the two types of sulphur defined above, or the concentration of sulphur reactive to cyanide ion.

EXPERIMENTAL

Preparation and chemical analysis of polysulphide solutions

Polysulphide solutions were prepared from elemental sulphur and sodium sulphide crystals by essentially the same procedures as those described by CLOKE.⁽²⁾ Three kinds of sodium polysulphide solution of approximately 1 N in Na⁺ concentration were used in this study.

For each preparation, the total sulphur, mono- and polysulphidic sulphur were determined by the conventional methods described elsewhere.^(3,3) The polysulphidic sulphur was also estimated from the amount of thiocyanate obtained by addition of an excess amount of potassium cyanide. Thio-sulphate and sulphate originally present in the solutions were also analysed in filtrates of the mixture

	PS-5	PS-7	PS-8
Total sulphur	57.75	59.25	36.58
Monosulphidic s.	14.65	16·27	16.24
Polysulphidic s.	2.94	2.64	1.25
Monosulphidic s.			
Sulphate sulphur	n.d.*	0.010	0.5
Thiosulphate sulphur	0.24	n.d.	n.d.
рН	12.8	13.0	13.2

TABLE 1.—SULPHUR COMPOSITION OF THE POLYSULPHIDE SOLUTIONS (mg S/ml)

* Not determined

of an aliquot of the solutions and an excess amount of acetate-buffered cadmium solution. The results of the sulphur analyses for the three polysulphide solutions are summarized in Table 1. The pH of the solutions measured by a glass electrode is also included in the Table.

Partial conversion of polysulphidic sulphur into thiocyanate

In order to measure the kinetic isotope effect in the reaction, polysulphidic sulphur of PS-7 and 8 was converted to thiocyanate in varying fractions up to completion and the isotope ratios, ³⁴S/⁸³S, of the total sulphur remaining as well as of the thiocyanate formed were determined.

The stock solutions of PS-7 and 8 were kept at 24.8°C for about 1 hr in a constant temperature bath to ensure isotope equilibration among all the sulphur species in the solutions. Then, a series of aliquots, 10 ml each, were pipetted from each of these into 20 ml glass stoppered measuring cylinders and varying amounts of solid potassium cyanide were added into them. The mixtures were shaken vigorously for a few minutes immediately after the addition of the salt and then kept standing for 30 min. The amounts of potassium cyanide were so adjusted that the fraction of the polysulphidic sulphur converted into thiocyanate should increase, from one after another in each series, by approximately 10 per cent of the completion, until in the last cylinder a slight excess of cyanide ion was present. In addition to these, a 5 ml aliquot was taken from each of the stock solutions and a large excess (approximately 10 times more than necessary for the complete reaction) of potassium cyanide was added in order to ensure the complete reaction.

The total sulphur remaining in each cylinder was then precipitated by acetate buffered cadmium solution and the precipitate filtered off the solution. The precipitate was oxidized to sulphate by

⁽²⁾ P. L. CLOKE, Geochim. cosmochim. Acta 27, 1265 (1963).

(8) G. SCHWARZENBACH and A. FISCHER, Helv. chim. Acta 43, 1365 (1960).

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bromine-nitric acid mixture and kept as barium sulphate for the isotope analysis. After evaporating the filtrate to near dryness with a small amount of sodium hydroxide, the thiocyanate in it was converted to sulphate by conc. nitric acid and weighed as barium sulphate. Only a few of the thiocyanate sulphurs in each series were subjected to the isotope analysis.

Isotope ratio measurements

The isotopic ratio of sulphur was measured by a mass spectrometer with a dual sample inlet and collection system similar to that described by MCKINNEY *et al.*⁽⁴⁾ and WANLESS and THODE.⁽⁵⁾ Barium sulphate and other forms of sulphur were converted into silver sulphide according to the procedures described by THODE *et al.*⁽⁶⁾ and the latter burnt to sulphur dioxide at 1200°C in a stream of oxygennitrogen mixture (1:20 v/v). The purified sulphur dioxide was then introduced into the mass spectrometer and the ³⁴S content was compared with that of a working standard sulphur dioxide. The results are reported in δ S values defined as follows:

$$\delta S(\%) = \left[\frac{({}^{34}S/{}^{33}S)_x}{({}^{34}S/{}^{32}S)_{st}} - 1\right] \times 1000$$

where x and st denote sample and standard, respectively.

Although the instrumental error in the isotope analysis was usually ± 0.1 per mil or less in δS scale at 95 per cent confidence level, a somewhat larger error was introduced during the chemical procedures as well as in the sample gas preparation. In order to obtain an idea of the overall reproducibility of the results, four 10 ml aliquots of PS-5 were completely reacted by excess potassium cyanide and the isotope ratio of thiocyanate and remaining sulphur (sulphide only in this case) was measured as described above.

RESULTS

In Table 2 are shown δS values of the four independently prepared pairs of sulphide and thiocyanate from PS-5 together with those of sodium sulphide and elemental sulphur used for the preparation of PS-5. The overall reproducibility is seen from the results to be $\pm 0.2 \sim 0.3$ per mil except for PS-5-2. In the pair mentioned, the δS value of the thiocyanate is too high.

No.	Sulphide	δS ‰ Thiocyanate	Isotope balance*
0†	+ 3.10		(+3.10)
1	$+ 23.9_{1}$	-4.3_{2}	$+2.9_{7}$
2	$+24.2_{2}$	-3.0^{-1}	$+3.9_{8}$
3	$+23.7_{6}$	-3.75	$+3\cdot3_{4}$
4	$+ 24 \cdot 1_{5}$	-3.72	+3.44
Na ₃ S‡ 1	+ 10.74)		
2	$+10.8_{0}$ av. 10.7_{0}		
3	+ 10.7		
element. s.‡	+ 0.0		

TABLE 2.—ISOTOPIC RATIO OF SULPHUR FROM PS-5

* Weighted mean of δS of sulphide and thiocyanate.

† Total sulphur of the original solution.

[‡] Na₃S and elemental sulphur used for the preparation of PS-5.

The results on PS-7 and 8 are summarized in Tables 3 and 4. When δS values are available for both the total sulphur and thiocyanate, their weighted means, or the isotope balances, are calculated. As seen from the Tables, the isotope balances are always found to be higher than the measured δS values of the original total sulphur. The reason for this discrepancy has not been clear to the present

⁽⁴⁾ C. R. MCKINNEY, J. M. MCCREA, S. EPSTEIN, H. H. ALLEN and H. C. UREY, *Rev. Sci. Instrumn.* 21, 274 (1950).

⁽⁵⁾ R. K. WANLESS and H. G. THODE, J. Scient. Instrumn. 30, 395 (1953).

⁽⁶⁾ H. G. Thode, J. Monster and H. B. DUNFORD, Geochim. cosmochim. Acta 25, 159 (1961).

	Total sulphur	δS ‰		Isotope
No.	not reacted (%)	$S'' + S_n''$	SCN'	balance
0	100.0	+2.74		(+3·4 ₀)*
1	93-4	+4·5 ₉	-18·9 ₄	+3.04
2	85·1	$+6.7_{1}$		
3	78.5	$+7.9_{0}$		
4	69.8	+10.70		
5	63.4	$+14.0^{\circ}$	-14·4 ₅	+3·5 ₉
6	55-1	+15.10		
7	48.9	+18.02		
8	40.1	$+21.1_{2}$		
9	31.7	+24.67	-6·2 ₈	+3.52
10†	27.5	$+22.6_{8}$	-3·8 ₈	+3.42
11†	27.5	+22.03	-	-

TABLE 3.—ISOTOPIC RATIO OF SULPHUR FROM PS-7

* The average of the isotope balances.

† The reaction completed by excess cyanide.

author, although it seems possible that during the chemical procedures the depletion of the lighter isotope took place owing to the formation of volatile sulphur compounds. However, the mutual consistency among the isotope balances within each series is satisfactory enough to support the view that no significant systematic error was introduced due to the unknown processes. In the following discussion, the average of the weighted means will be used for the δS value of the original total sulphur instead of the measured one.

These results show that there is a fairly large kinetic isotope effect in the reaction studied, the heavy isotope being enriched in the remaining sulphur chains as expected. The apparent enrichment factors as large as 1.033 in PS-7-9 and 1.021 in PS-8-5 are attained between thiocyanate and total sulphur. However, significantly smaller effects are observed in the last two samples in both series, where the reaction is completed by a slight excess (PS-7-10 and PS-8-6) or a large excess of cyanide. It is also apparent that the rate of increase of the integrated isotope effect, especially in PS-8, tends to decrease as the reaction proceeds toward completion. This is better shown in Fig. 1, where the isotope ratios are plotted against the ratios of total sulphur to monosulphidic sulphur (both in log-scale).

	Total sulphur	δS ‰		Isotope	
No.	not reacted (%)	$S'' + S_n''$	SCN'	balance	
0	100.0	+4·5 ₆		(+5·0 ₈)*	
1	90.2	+6.86			
2	80.6	+9.4,	-13·14	+5.08	
3	69·1	$+11.6_{1}$			
4	58.5	$+13.9_{8}$			
5	49.6	+15.4	-5·4 ₃	+4·91	
6†	44 ·8	$+13.7_{1}$	-1.8,	$+5.1_{0}$	
7†	44 ·8	$+14.6_{1}$		•	

TABLE 4.—ISOTOPE RATIO OF SULPHUR FROM PS-8

* The average of the isotope balances.

† The reaction completed by excess cyanide.

DISCUSSION

The rate of the accumulation of the heavy isotope in the polysulphide chain (and sulphide) and of the light isotope in thiocyanate is determined by the kind of ionic species present in the solution and the overall reaction mechanism. The isotope

exchange between polysulphide and thiocyanate as well as that between sulphide and thiocyanate can be ignored, as KOROS *et al.*⁽¹⁾ found no measureable exchange of radiosulphur between them.

From their recent study on the protonation constants of alkali polysulphides, SCHWARZENBACH and FISCHER⁽³⁾ presented strong support to the view against the presence of di- and tri-polysulphide ions in aqueous solution. These ions are instantly



FIG. 1. Variation of the sulphur isotope ratio during the course of reaction. The amount of the monosulphidic sulphur is assumed constant. The slope of the solid lines represents Equation (9').

disproportionated into sulphide, tetra- and penta-polysulphide and the chemical equilibrium among these ions is established within a fraction of a second as shown below:

$$4 S_4'' + H_2 O \rightleftharpoons OH' + SH' + 3 S_5''$$
⁽²⁾

This equilibrium reaction should also establish the rapid isotope exchange of sulphur among them as already found by KOROS *et al.*,⁽¹⁾ CLOKE⁽²⁾ also concluded that S_6'' is present in a less significant amount based on his pH-Eh measurements on sodium polysulphide solutions.

From these observations, the schematic process of the reaction may be written as follows:

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 $[S-S-S-S]'' + CN' \xrightarrow{k_1} [S-S-S]'' + SCN'$ (3)

$$*[S-S-S-S]'' + CN' \xrightarrow{k_1} [S-S-S]'' + *SCN'$$
(4)

$$\underset{k_*}{\overset{}{\vdash}} *[S-S-S]'' + SCN'$$
 (5)

where the asterisk denotes a molecule of a heavy isotope, and k the specific rate constant. The trimers formed will be further attacked by cyanide or will disproportionate into the above mentioned three species:

$$3 S_3'' + H_2 O \rightarrow 2 S_4'' + SH' + OH'$$
 (6)

or

or

$$S_3'' + 2 CN' \rightarrow S'' + 2 SCN'$$
⁽⁷⁾

In this case, the isotope effect will vary depending on which type of the reactions is predominant. In addition, the actual reaction mechanism may be more complicated.

At the beginning of the reaction, however, the isotopic ratio of sulphide ion does not determine that of total sulphur and of polysulphide ions. This implies that the kinetic isotope effect measured by the thiocyanate sulphur obtained at the beginning of the reaction can be used to estimate the *apparent* kinetic isotope effect in the formation of thiocyanate, or $k_1/\beta k_2$ in which β represents the number of sulphur atoms in a polysulphide chain playing an equivalent role in the rate determining step of the reaction. Assuming that the reaction is first-order in polysulphide ions, $k_1/\beta k_2$ can be estimated by the Equation (8):

$$\frac{k_1}{\beta k_2} = \frac{R_p^0}{R_{th}} \tag{8}$$

where R_p^0 denotes the isotopic ratio, ³⁴S/³²S, of polysulphide ions in the original solution and R_{th} that of thiocyanate obtained at the beginning of the reaction. When polysulphide ions are in isotopic equilibrium with sulphide ion, R_p^0 can be related to the isotopic ratio of total sulphur in the original solution, R_t^0 , and that of sulphide, R_s^0 , as follows:

$$R_t^{0} = R_p^{0}(1/\alpha + nx_p)/(1 + nx_p)$$

where α is the elementary separation factor of sulphur isotopes, $\frac{R_p^0}{R_s^0}$, *n* the number of sulphur atoms in a polysulphide ion, and x_p the molecular ratio of polysulphide to sulphide ions. Introducing the above relation into the Equation (8), the kinetic isotope effect can be expressed as follows:

$$\frac{k_1}{\beta k_2} = \frac{R_t^0}{R_{th}} \cdot \frac{(1+nx_p)}{(1/\alpha+nx_p)} \tag{8'}$$

Using R_{th} at zero reaction extrapolated from the observed values (see Fig. 1) and R_t^0 (the average of isotope balance), the kinetic isotope effect can be calculated to be 1.022 for PS-7 and 1.021 for PS-8, respectively. The effect of α , up to 1.03, can be ignored in both cases because nx_p is sufficiently large.

Under the assumption of a first-order reaction, the differential isotope effect may be approximately expressed as follows:

$$d^*\mathbf{S}_t / d\,\mathbf{S}_t = \beta k_2 / k_1 \cdot R_p \tag{9}$$

$$d\ln R_t / d\ln S_t = (\beta k_2 / k_1 \cdot A - 1) \tag{9'}$$

where $*S_t$ and S_t represent the atomic concentration of the heavy and light isotopes of sulphur in total sulphur at a stage of the reaction, R_p and R_t the isotopic ratio of polysulphide and total sulphur at the stage, and $A = (1 + nx_p)/(1/\alpha + nx_p)$. The solid lines in Fig. 1 represent Equation (9') with $\beta k_2/k_1 = 1/1.022$ as estimated above.

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The measured points in an earlier stage of the reaction fit the line quite well in both cases, implying that the reaction is actually first-order in this region. Because the amount of cyanide is deficient at this stage, the reaction such as shown in Equation (7) would not be important. Therefore, the estimated isotope effect could be taken as that involved in such reactions as shown in Equations (3) and (4).

The deviation of the observed data from the line becomes significant as more cyanide is added. This is apparently due to a combined effect of an increasing importance of α , non-equilibration between sulphide and polysulphide and variation in the apparent kinetic isotope effect itself owing to some other types of reaction mechanisms such as shown in Equation (7). Although detailed discussion of these effects is not possible at present, it is clear from the present results that the reaction rate is mostly controlled by the S—S breaking step.