Isomerization of Thiourea to Ammonium Thiocyanate and Isotopic Exchange between [^{35}S]Thiourea and Diphenyl Tetrasulphide

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The specific rate of isomerization of thiourea to ammonium thiocyanate has been determined at 120° in 1 : 1 ethanol–xylene and in ethanol–benzene by radiochromatography using ^{35}S-labelled thiourea. The isotopic exchange between [^{35}S]thiourea and diphenyl tetrasulphide in 1 : 1 ethanol–xylene, studied by radiochromatography, shows that the tetrasulphide exchanges only one sulphur atom with thiourea at 100° and two sulphur atoms at 120°. The rate constant for exchange [k_2 $9{\cdot}57{\cdot}10^{-7}$ l (g-atom)$^{-1}$ s^{-1}] could only be determined at 100° because at 120° the rate of isomerization of thiourea was too high.

The mobility of sulphur atoms in a chain in polysulphides has been studied using a ^{35}S label either in synthesis or in isotopic exchange reactions of organic and inorganic polysulphides. At 100°, the radioactive trisulphide EtS–S*–SEt exchanges its radioactive sulphur only with the central sulphur atoms of diethyl tetrasulphide, but no exchange was observed between the central and terminal sulphur atoms[1] below 210°. Organic polysulphides exchange their terminal groups attached to radioactive sulphur without any exchange of the sulphur atom.[2]

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[1] E. N. Gur'yanova, Y. K. Sirkin, and L. S. Kuzina, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **86**, 107.

[2] E. N. Gur'yanova and V. N. Vasilieva, *Khim. Seraorgan. Soedinenii, Soderzhashch. v Neft. i Nefterprod., Akad. Nauk S.S.S.R., Bashkirsk. Filial*, 1961, **4**, 24.

Thiourea and substituted thioureas exchange their sulphur atom with ^{35}S but at much higher temperatures and over much longer periods than are required by the central sulphur atoms of organic polysulphides.[3] These exchange reactions can be used to prepare ^{35}S-labelled thioureas.

Owing to the reactivity of the thiourea C=S group, the present investigation was undertaken in order to examine the possibilities of isotopic exchange between [^{35}S]thiourea and diphenyl polysulphides.

EXPERIMENTAL

Reagents.—Diphenyl sulphide (Fluka), b.p. 96—100° at 0·1 mmHg, was used as received. Diphenyl disulphide (Fluka) was recrystallized from ethanol, m.p. 58—60°. Diphenyl tetrasulphide, prepared[4] from thiophenol and sulphur monochloride, was purified by chromatography on neutral alumina (Merck), m.p. 112° (from xylene) (Found: C, 50·9; H, 3·6; S, 45·2. Calc. for $C_{12}H_{10}S_4$: C, 51·0; H, 3·5; S, 45·2%). Pure diphenyl trisulphide could not be prepared. ^{35}S-Labelled thiourea (Sorin, Saclay) was isotopically diluted with inactive thiourea (C. Erba) to obtain a 0·2M solution in ethanol.

TABLE 1

Kinetics of the isomerization $*SC(NH_2)_2 \longrightarrow NH_4*SCN$ at 120 ± 0·1° in a mixture of equal volumes of 0·2M-$*SC(NH_2)_2$ in EtOH and 0·2M-Ph_2S (or Ph_2S_2) in benzene or xylene

	Ph_2S–EtOH–benzene		Ph_2S–EtOH–xylene		Ph_2S_2–EtOH–benzene		Ph_2S_2–EtOH–xylene	
t/h	$*SCN^-$ (%)	$10^6\ k/s^{-1}$	$*SCN^-$ (%)	$10^6\ k/s^{-1}$	$*SCN^-$ (%)	$10^6\ k/s^{-1}$	$*SCN^-$ (%)	$10^6\ k/s^{-1}$
5	4·53	2·57	4·17	2·37				
7	6·26	2·57	6·24	2·56	5·70	2·33	6·67	2·74
10	8·42	2·44	8·18	2·37	9·00	2·62	9·40	2·77
15	(10·52)		13·14	2·61	12·20	2·39	13·93	2·78
20			16·20	2·46	16·03	2·43	18·16	2·78
25			19·91	2·47	19·29	2·38	21·89	2·75
Average		2·53		2·47		2·43		2·77

Total average 2·55 ± 0·20.

Equal volumes of a xylene solution of diphenyl sulphide, diphenyl disulphide (0·2M), or diphenyl tetrasulphide (0·1M), and of an ethanolic solution of [^{35}S]thiourea, mixed and sealed in glass vessels, were heated in an oil-bath at the reaction temperature, for the times indicated. Then the solutions were quenched at room temperature. Using 10 μl of the solution, the products were separated by ascending chromatography on Whatman No. 1 paper strip (8 × 350 mm) using water saturated with carbon tetrachloride as the eluting phase. Products, with their R_F values, are given in Table 2.

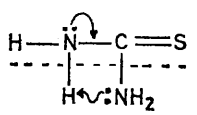
The radioactivity of the chromatographs was measured by direct scanning of the paper strip mounted on a sliding base which was moved across the end-window of a Geiger–Muller counter, to which a lead mask with a rectangular 10 × 15 mm slit was applied. Standard electronic equipment was used with the counter tube mounted in a universal lead castle. The usual allowance was made for background (*ca.* 10 counts min^{-1}).

RESULTS AND DISCUSSION

In the temperature range 100—120° no isotopic exchange was observed between [^{35}S]thiourea and diphenyl sulphide or diphenyl disulphide in ethanol–benzene or ethanol–xylene (1 : 1). Only radioactive thiourea and ammonium thiocyanate, due to the isomerization of thiourea, were detected in these systems. The amount of radioactive thiocyanate at 100° is <1% after 25 h, while at 120° it is *ca.* 20% after the same time.

The specific rate of the isomerization of thiourea to ammonium thiocyanate was determined in 1 : 1 ethanol–xylene and ethanol–benzene at 120° assuming a first-order reaction[5] (Table 1). The calculated isomerization constant (k 2·5 × 10^{-6} s^{-1}) is in good agreement with that measured at 120° in water solution (1·97 × 10^{-6} s^{-1}) by Shaw and Walker.[5] This supports the view of these authors that water does not take part in the isomerization mechanism of thiourea which should therefore involve only an intramolecular rearrangement of type A.

Isotopic exchange between [^{35}S]thiourea (0·1M) and the diphenyl tetrasulphide (0·05M) in xylene–ethanol (1 : 1) occurs at 100 and 120° as indicated in Table 2. The exchange values obtained at 100° are not seriously affected by thiourea isomerization, unlike those at 120°, and were used for the determination of the rate constant for exchange k_2.



A

TABLE 2

Exchange reaction in ethanol–xylene (1 : 1) between [^{35}S]thiourea (0·1M) and diphenyl tetrasulphide (0·05M) at 100 and 120°

		Partition of radioactivity (%)		
	t/h	Thiourea	Sulphide	Thiocyanate
100°	5	86·56	13·44	
	10	78·51	21·49	
	15	73·69	26·31	
	20	70·45	29·10	0·45
	25	68·32	30·80	0·88
120°	1	83·53	15·73	0·74
	2	72·36	26·34	1·29
	3	64·74	33·58	1·68
	4	59·55	38·34	2·11
	5	55·98	41·48	2·54
	6	53·47	43·54	2·99
	8	50·38	45·85	3·77
R_F		0·71	0·00	0·85

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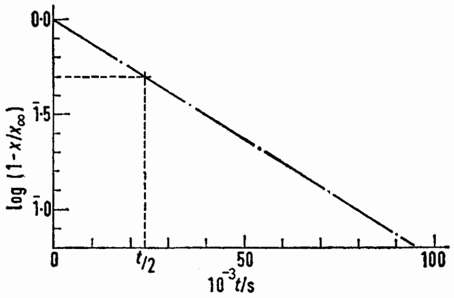
[3] E. N. Gur'yanova, *Zhur. fiz. Khim.*, 1954, **28**, 67.

[4] H. Lecher, *Ber.*, 1925, **58**, 417.

[5] W. H. R. Shaw and D. G. Walker, *J. Amer. Chem. Soc.*, 1956, **78**, 5769.

A plot of the percentage radioactivity of the tetrasulphide against the reaction time shows that the exchange tends to a limit of 33% at 100° and of 50% at 120° for the same concentration and ratio (2 : 1) of thiourea and diphenyl tetrasulphide in the same solvent. This seems to indicate that at 100° only one sulphur atom and at 120° two sulphur atoms of the tetrasulphide can exchange.

For the exchange process $Ph_2S_4 + {}^*SC(NH_2)_2 \rightleftharpoons Ph_2S_4{}^* + SC(NH_2)_2$ at 100° let $[Ph_2S_4] + [Ph_2S_4{}^*] = a$, $[{}^*SC(NH_2)_2] + [SC(NH_2)_2] = b$, $[Ph_2S_4{}^*] = x$, and $[SC(NH_2)_2] = y$ with $k_2 =$ the rate constant (hence $b = 2a$) the rate equation (1) [6] is obtained which



Variation of log $(1 - x/x_\infty)$ with time for the exchange reactions $(NH_2)_2CS{}^* + Ph_2S_4 \rightleftharpoons (NH_2)_2CS + Ph_2S{}^*_4$ in ethanol–xylene (1 : 1) at 100°

$$dx/dt = (3k_2/2a)(x_\infty - x) \qquad (1)$$

integrates to (2), the usual form of the first-order rate

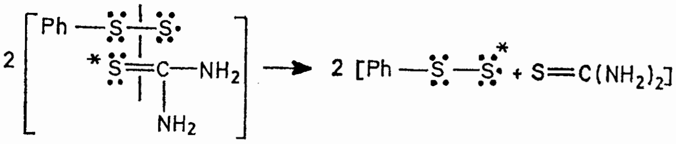
$$-\ln\left[1 - (x/x_\infty)\right] = 3k_2t/2a \qquad (2)$$

law.[6] From a plot of $\log[1 - (x/x_\infty)]$ *versus* time (Figure) the half-time (6·67 h) and the exchange rate constant [$9{\cdot}57 \times 10^{-7}$ l (g-atom)$^{-1}$ s^{-1}] were determined. The higher values of the isomerization of thiourea to ammonium thiocyanate at 120° (Table 2) did not allow the exchange rate constant at this temperature to be evaluated. The different percentage limits of radioactivity to which, with the same ratio of [^{35}S]thiourea, diphenyl tetrasulphide tends at equilibrium, indicate different modes of exchange.

It has been observed [1,7,8] that ethyl tetrasulphide, which is thermally less stable than the trisulphide, exchanges both the central sulphur atoms at 95—100° with the radioactive central sulphur atom of the trisulphide. It was not possible on the basis of this exchange to choose between the linear and branched structures for the tetrasulphide.[1] Though some authors deny that the branched form can be considered normal [9] owing to the instability of co-ordinate and double bonds between sulphur atoms, the branched form has been invoked as an intermediate in some rearrangement mechanisms.[10]

The exchange reaction between labelled thiourea and diphenyl tetrasulphide at 100° seems to occur by a bimolecular mechanism $(NH_2)_2CS{}^* + Ph_2S_4 \rightleftharpoons (NH_2)_2CS + Ph_2S_4{}^*$. This exchange mechanism may involve an intermediate branched form or nucleophilic attack by thiourea on a positively charged internal sulphur atom.

The exchange reaction at 120°, on the other hand, seems to occur as a result of a symmetrical cleavage of the tetrasulphide into two Ph_2S_2 radicals [8] each exchanging its terminal sulphur atom with labelled thiourea with a mechanism of the type shown in the Scheme.



SCHEME

Owing to the fact that the central S–S bond of the tetrasulphide is longer [11] and weaker [12] than the other two this mechanism is quite reasonable.

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[3/1948 *Received, 24th September,* 1973]

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[6] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' Wiley, London, 1963, p. 192.

[7] D. Twiss, *J. Amer. Chem. Soc.*, 1927, **49**, 491.

[8] T. L. Pickering, K. I. Saunders, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1967, **89**, 2364.

[9] O. Foss, *Acta Chem. Scand.*, 1950, **4**, 404.

[10] D. Barnard, T. H. Houseman, M. Porter, and B. K. Tidd, *Chem. Comm.*, 1969, 371.

[11] S. C. Abrahams, *Acta Cryst.*, 1954, **7**, 423.

[12] I. Kende, T. L. Pickering, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1965, **87**, 5582.