

Appendix

In general, if a practical osmotic coefficient, ϕ , is measured, it can be converted to the activity coefficient of the solute, γ_{\pm} , by using the Gibbs–Duhem relationship. That is

$$d\{m(1 - \phi)\} + m d \ln \gamma_{\pm} = 0 \quad (32)^{23}$$

where m is the molal concentration of the solute. Integration of eq. 32 with the assumption of eq. 24 gives

$$\ln \frac{(\gamma_{c^+})_{m_1}}{(\gamma_{c^+})_{m_2}} = (\phi_{m_1} - \phi_{m_2}) - 2 \int_{m_1}^{m_2} \left(\frac{1 - \phi}{m^{1/2}} \right) dm^{1/2} \quad (33)^{24}$$

If we apply this relationship to polyelectrolyte solutions

and insert the experimental values of ϕ into eq. 33 to calculate γ_{c^+} , the calculated values are not only in numerical disagreement with values determined by other direct methods but also show a concentration dependence quite different from the experimental one. Although the contribution of the polyion to the chemical potential of the polyelectrolyte component is assumed to be negligible compared with the contribution of the counterion, and, also, the calculation of γ_{c^+} involves the assumption that $\gamma_{K^+} = \gamma_{Cl^-}$ in KCl solutions, it is inconceivable that these assumptions cause this contradiction, so far as our discussion is limited to a ratio of the activity coefficients at two different concentrations, $(\gamma_{c^+})_{m_1}/(\gamma_{c^+})_{m_2}$. At present, we have no idea of the origin of this contradiction.

[CONTRIBUTION FROM THE MONSANTO COMPANY, CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI]

Exchange of Parts between Molecules at Equilibrium. V. Alkyl-Terminated Chain Polysulfides and Polyselenides

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The proton nuclear magnetic resonance chemical shift of appropriate alkyl end groups for polysulfides (*i.e.*, sulfanes) or polyselenides (*i.e.*, selenanes) varies with the length of the sulfur or selenium chain, reaching in any particular solution or mixture a constant value for the very long chains. Thus the smaller molecules containing from a single sulfur or selenium atom up to six or ten such atoms may be quantitatively measured in mixtures. This technique has been employed to study the equilibria between variously sized chains in the reorganizing systems obtained by mixing various proportions of elemental sulfur with either dimethyl or di-*t*-butyl disulfide. In addition to a study of the kinetics of this equilibration process, the method was also applied to the investigation of the course of condensation polymerization between dialkyl and dichloro sulfides or selenides to form the alkyl chloride plus the respective sulfide or selenide chains. A study was also made of the reaction between dimethyl sulfide and elemental sulfur—a reaction which gives complicated mixtures consisting of the dialkyl polysulfides as well as methyl-terminated methylene sulfide chain molecules.

Primarily due to the work of Feher and colleagues,² a great deal is known about various molecules based on chains of sulfur atoms terminated by a variety of monofunctional substituents. However, the unique capability inherent in nuclear magnetic resonance (n.m.r.) for simultaneously identifying and carrying out a quantitative assay of individual species in complicated mixtures of molecules³ has not previously been applied to this chemistry to which the technique is so well suited. N.m.r. is a particularly useful tool in the study of polysulfides (also called α,ω -disubstituted sulfanes) and polyselenides (also called α,ω -disubstituted selenanes) because these systems are sufficiently labile so that quantitative conclusions based on classical separations methods for molecules automatically become suspect.

Another reason for carrying out this study was to extend the broad investigation of equilibrium chemistry now underway in this laboratory³ to the molecules having –S–S– chains in their backbone. Since the achievement of disproportionation equilibrium between two symmetric alkyl disulfides to give the corresponding mixed one has been demonstrated,⁴ equilibration be-

tween a range of different sizes of alkyl polysulfides is to be expected.

Experimental

Reagents.—Sulfur dichloride obtained from Matheson Coleman and Bell was taken from fresh bottles which had not been opened until being placed in a drybox. Dimethyl sulfide and *t*-butyl disulfide were procured from Columbia Chemical Co., of Columbia, S. C. Dimethyl disulfide and dibenzyl disulfide came from Eastman Kodak Co. and the Waterlee Chemical Co. of Lugoff, S. C., respectively. The 2,2'-dithiobisbenzothiazole was a recrystallized sample from the Monsanto Chemical Co., and the elemental sulfur was a precipitated U.S.P. grade bearing the Baker and Adamson reagent chemical label.

Dimethyl diselenide (*i.e.*, methyl selenide) and dichloro diselenide (*i.e.*, selenium monochloride) were purchased from Metallomer Laboratories, Maynard, Mass., and Peninsular Chemical Research, Gainesville, Fla., respectively. Dimethyl selenide was prepared by modification of a published procedure,⁵ a modification in which the stated proportion of reagents was mixed with cooling and the reaction mixture was then stirred at room temperature for 1 week. The n.m.r. analysis for hydrogen-containing substituents as well as standard wet-chemical procedures for sulfur and selenium showed that the compounds prepared by us and those purchased on special order from the custom manufacturers were free from gross amounts of impurities.

Reactions.—Equilibration studies of mixtures of dimethyl or di-*t*-butyl sulfide with elemental sulfur were carried out in 5-mm.

(1) Postdoctoral Fellow from the University of Glasgow, Sept., 1962–1963.

(2) F. Fehér, Special Publication, No. 12, The Chemical Society, London, 1958, p. 305 [Chemical Society Conference, "Recent Work on the Inorganic Chemistry of Sulfur," Bristol, England]. Also see M. Schmidt, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, Inc., New York, N. Y., pp. 98–158.

(3) See papers I, II, and IV in this series; *i.e.*, K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802, 807, 814 (1964).

(4) L. Haraldson, C. J. Olander, S. Sunner, and E. Varde, *Acta Chem.*

Scand., **14**, 1509 (1960). For other similar exchange reactions, see C. A. M. Mauritzen and P. Stewart, *Nature*, **197**, 48 (1963), and K. W. Bowers, *Dissertation Abstr.*, **23**, 1512 (1962). A related mechanism study is given by A. J. Parker and N. Kharasch, *J. Am. Chem. Soc.*, **82**, 3071 (1960), and related thermodynamic data by W. D. Good, J. L. Lancina, and J. P. McCullough, *J. Phys. Chem.*, **65**, 860 (1961).

(5) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 572 (1942).

TABLE I
 H^1 CHEMICAL SHIFTS (IN P.P.M.) OF SOME ORGANIC POLYSULFIDES AND POLYSELENIDES

	Values of n									
	1	2	3	4	5	6	7	8	9	10
$CH_3S_nCH_3^a$	-2.159	-2.375	-2.521	-2.615	-2.632	-2.663	(-2.688) ^b	(-2.707)	(-2.722)	(-2.726)
CH_3S_nCl	-6.833	-5.667	-5.333	-5.033	-4.833	-4.750			-4.167	
$(CH_3)_3CS_nC(CH_3)_3^a$		-1.268	-1.337	-1.368	-1.381	-1.392	(-1.400) ^b	(-1.407)	(-1.414)	(-1.419)
$C_6H_5CH_2S_nCH_2C_6H_5$		-3.683	-3.883	-4.067	-4.200	-4.300	-4.333			
$CH_3Se_nCH_3$	(-6.67)	-5.583	-4.517	-4.300	-3.717	-3.693				
CH_3Se_nCl	-2.333	-2.733	-2.990	-3.100	-3.167	-3.258				

^a Referenced to internal tetramethylsilane; all others externally referenced to the same standard. ^b Values in parentheses are extrapolated; see Fig. 1.

sealed precision-bore Pyrex n.m.r. tubes containing carefully apportioned quantities of the reagents. These tubes were kept in a forced-draft drying oven, with good temperature control, set at 118°. Analyses were carried out periodically by quickly cooling the tubes to room temperature, running the n.m.r. spectra, and returning the tubes to the oven. With an over-all ratio of $CH_3/S < 0.5$ in the reaction mixture, yellow sulfur crystallized out of the mixture at room temperature; however, the crystallization process was sufficiently slow so that n.m.r. spectra could always be obtained on supercooled liquids containing no solid. Although there was a regular increase in viscosity with increasing sulfur content, the room-temperature viscosity was never sufficiently great so as to broaden the n.m.r. peaks to the point where they were hard to recognize or quantitative measurements of area could not be made.

In the study of condensation polymerization, carefully measured amounts of the appropriate monomer or dimer were slowly mixed in test tubes in a drybox or glove bag. After the initial fast evolution of volatile alkyl chloride (in cases where this occurred), the samples were transferred to precision-bore 5-mm. n.m.r. tubes, closed with tight-fitting polyethylene stoppers, and studied by recording the n.m.r. spectra from day to day at room temperature. When evolution of a volatile alkyl chloride continued slowly over a period of several days, the stoppers were removed at intervals in a dry atmosphere. When phase separation occurred, the two phases were separated and studied individually. When a solid was formed during the reaction, it was treated with carbon disulfide, and the n.m.r. spectra of the resulting solution obtained. The volatilization of alkyl chloride was followed quantitatively by periodic weighings.

The reaction of dimethyl sulfide with elemental sulfur was studied by heating carefully measured amounts of the reagents in sealed n.m.r. tubes under a variety of time and temperature conditions. In carrying out kinetic studies on this system, the tubes were rapidly cooled to room temperature and the n.m.r. spectra taken immediately thereafter.

Analytical Procedure.—A Varian A-60 high-resolution spectrometer was used for analyses. Quantitative data were obtained from the methyl protons of the *t*-butyl and methyl substituents and from the methylene protons of the benzyl group. The majority of the quantitative spectra were run at a sweep rate of 0.1 c.p.s., using the widest sweep width (50 cycles for the entire scale). Areas were measured with the built-in electronic integrator and by cutting out and weighing Xerox copies of the spectra. Chemical shifts are reported with respect to tetramethylsilane, with negative shifts being downfield.

The n.m.r. peaks were generally assigned to specific molecular structures on the basis of their variation as a function of time and the over-all stoichiometry of the reaction mixture. A series of peaks starting with the mono- or disulfide or mono- or diselenide (depending on the starting materials) and exhibiting chemical shifts lying closer and closer together up to a limiting value were observed in those systems in which the sulfur or selenium chains were terminated at both ends by the same substituent. However, for systems in which two kinds of terminating substituents were available (*e.g.*, condensation polymers obtained from mixtures of $(CH_3)_2S$ and SCl_2) more than one such series of n.m.r. peaks was seen, corresponding to the various possible combinations of terminal groups on the chains. As shown in Table I, these series of peaks were assigned to the end groups of the sequence of progressively longer chains ranging up to those exhibiting 6–10 sulfur or selenium atoms per chain (depending on the particular system). Although the resonances corresponding to the longer chains were only partially resolved or had even coalesced completely, semiquantitative data could be obtained

for the relative amounts of these chains by an extrapolative graphical procedure, as shown in Fig. 1.

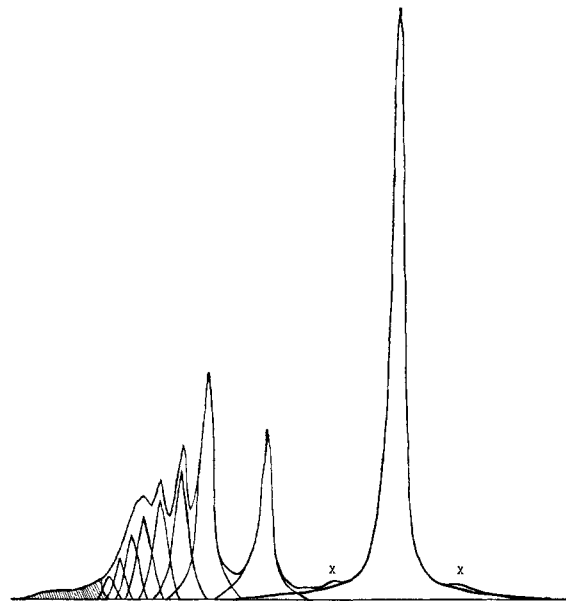


Fig. 1.—Proton n.m.r. spectra of an equilibrated mixture of di-*t*-butyl disulfide with sulfur for the value of $R \equiv (CH_3)_3C/S = 0.48$. This figure shows how the spectra are divided into individual resonance peaks. The two peaks marked X are satellites attributable to C^{13} coupling in the disulfide (major peak).

The positions of the n.m.r. peaks relative to each other remained practically constant for a given series over the range of stoichiometry studied and upon addition of various solvents; but the position relative to tetramethylsilane of a series was observed to shift by as much as 0.5 p.p.m. through changes in stoichiometry or use of a solvent. Obviously, the chemical shifts of the various materials listed under Reagents were obtained on the pure samples and could be used in identifying their presence in mixtures. A preliminary communication concerning these chemical shifts has already been published.⁶

Results and Interpretation

Kinetics of Equilibration of Dialkyl Disulfide⁷ with Sulfur.—At 120°, elemental sulfur was found to dissolve within a few hours in dimethyl disulfide and within several weeks in di-*t*-butyl disulfide. A number of kinetic studies were carried out, as illustrated by Fig. 2. Although data were obtained at only a few widely spaced times, the curves shown in this figure are well defined because of the material-balance requirement of keeping the CH_3/S mole ratio constant.

From these kinetic studies, it was found that equilibrium was reached in the case of the CH_3SSCH_3 vs. S_8 system in a period ranging from 5 days for an over-all mole ratio $R \equiv CH_3/S = 0.8$ to 40 days at $R = 0.2$,

(6) J. R. Van Wazer and D. Grant, *J. Am. Chem. Soc.*, **86**, 1450 (1964).

(7) For other data on the dialkyl polysulfides (sulfones) see F. Fehér, G. Krause, and K. Vogelbruch, *Chem. Ber.*, **90**, 1570 (1957).

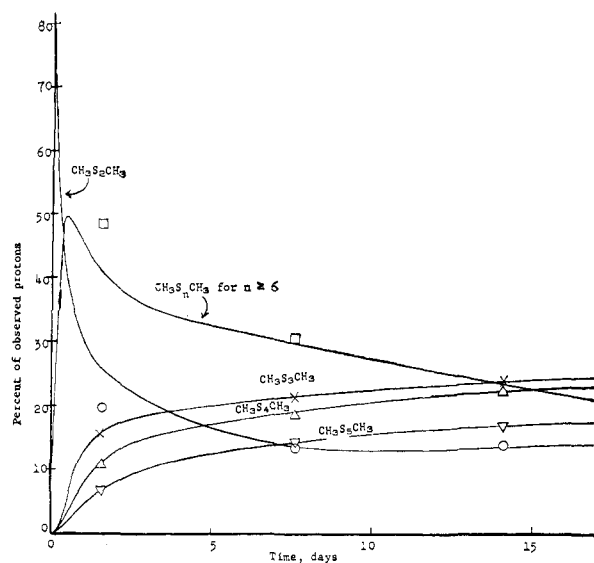
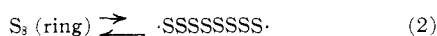


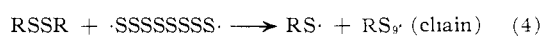
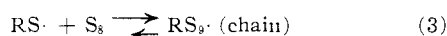
Fig. 2.—Variation with time in the percentage of the total protons corresponding to the species indicated, for an over-all CH_3/S mole ratio of 0.47 in the equilibration of dimethyl disulfide with elemental sulfur at 120° . The percentage of total protons corresponding to a given molecule in this system equals the percentage of total chains present as the given compound.

with a continuous decrease in rate with decreasing R -value. Likewise, for the $(\text{CH}_3)_3\text{CSSC}(\text{CH}_3)_3$ vs. S_8 system, the rate of equilibration was also found to decrease with decreasing R -value. The major difference between the systems based on methyl-terminated and t -butyl-terminated sulfur chains is that the elemental sulfur dissolves slowly in the t -butyl system at elevated temperatures below the transition^{8,9} from S_8 rings to free-radical-terminated chains in pure sulfur. It is interesting to note that shaking for a minute or two causes a rapid diminution in the amount of sulfur-rich phase in the case of the methyl-terminated system but not in the t -butyl one.

In the series of kinetic runs (exemplified by Fig. 2) using various starting proportions of dialkyl disulfide to sulfur, two rate processes were readily distinguished. The initial rapid one involves the opening of the S_8 rings to form relatively long alkyl-terminated chains which then undergo the subsequent process of exchanging parts with each other to give the final dynamic equilibrium distribution of molecular species corresponding to the particular over-all stoichiometry. In accord with the present consensus¹⁰ that reactions of this type proceed *via* a free-radical mechanism, initiation of the reaction may be attributed to the equilibria of either eq. 1 or 2.



As part of the first rate process, we have

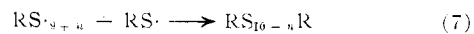
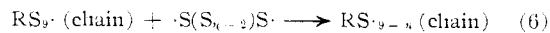


(8) R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943).

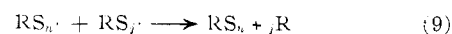
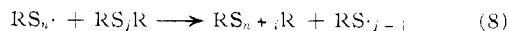
(9) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952); also see R. E. Powell and H. Eyring, *J. Am. Chem. Soc.*, **65**, 648 (1943).

(10) E. g., D. M. Gardner and G. K. Fraenkel, *ibid.*, **76**, 5891 (1954); F. K. Truby, *J. Chem. Phys.*, **36**, 2227 (1962).

In addition, a large proportion of sulfur in the reagent mixture or choice of conditions leading to an increase in the amount of free-radical-terminated sulfur chains will give reactions of the type



Concomitant and subsequent to these reactions, there are the ones whereby the equilibrium between the various sized molecules is achieved, *i.e.*



For the run on the methyl system represented in Fig. 2, where to start there were about four molecules of dimethyl disulfide per S_8 molecule, material-balance calculations showed that the n.m.r. peak representing the sum of all chain molecules exhibiting six or more sulfur atoms corresponded to only six sulfurs per chain with no free sulfur (*i.e.*, no S_8) by the time the first set of experimental points were taken. Since the sulfur-rich phase was caused to disappear by shaking when the tube was removed from the 120° oven to obtain the first set of points (at which time the resulting single-phase liquid was very mobile), it is seen that the reactions of eq. 1–5 proceeded to completion in a liquid two-phase system with minimal formation of long chains by eq. 6 and 7. The section of Fig. 2 prior to the first experimental point is drawn on this basis.

In addition to the initial rapid increase in the number of long chains, all of the kinetic runs showed an early buildup of tri-chains. The simplest explanation for this finding is a preferential attack by the smaller radicals on portions of the longer molecules toward the chain ends (eq. 8). Addition of small amounts of a free-radical-promoting catalyst—2,2'-dithiobisbenzothiazole, Thiofide—greatly increased the rate of formation of long chains according to eq. 6 and 7 so that in a matter of a few hours at 120° , the entire mass converted into a viscous gel. This gel formation inhibits the subsequent degradation of the long chains to the equilibrium mixture, presumably through the introduction of diffusion control to the reactions of eq. 8 and 9. Naturally this effect varies with the amount of the promoter employed and the initial ratio of dimethyl disulfide and elemental sulfur.

Since the rate of diminution of the sulfur-rich phase was quite slow in the t -butyl system, both phases could be conveniently studied in a high-temperature n.m.r. probe. For a period ranging from several hours to several days at 120° , t -butyl end groups exhibiting chemical shifts corresponding to the very long chains were seen to be present in the sulfur-rich phase. This observation emphasizes the possibilities for complicated mechanistic behavior at the beginning of the reaction when the two phases are present. One might postulate, for example, that the long t -butyl terminated chains dissolved in the sulfur are produced by an interaction between t -butyl disulfide and the small amount of free-radical terminated long sulfur chains adduced⁹ to be present in small amounts along with the S_8 rings in sulfur at this temperature.

Equilibrium between S_8 Rings and RS_nR Chains.—By mixing various proportions of dialkyl disulfides with elementary sulfur, a dynamic equilibrium with

TABLE II

MOLE PERCENTAGE OF VARIOUS MOLECULES FOUND AT EQUILIBRIUM IN MIXTURES OF DIMETHYL DISULFIDE WITH SULFUR AT 120°

$-R = \text{CH}_3/\text{S}-$						
From ingredients	From n.m.r. data	$\text{CH}_3\text{S}_2\text{CH}_3$	$\text{CH}_3\text{S}_3\text{CH}_3$	$\text{CH}_3\text{S}_4\text{CH}_3$	$\text{CH}_3\text{S}_n\text{CH}_3$	$\text{CH}_3\text{S}_n\text{CH}_3$ for $n \geq 6$
0.90	0.87	75 (81.8) ^a	21 (14.9)	3 (2.7)	1 (0.5)	0 (0.1)
.89	.87	75 (80.2)	22 (15.9)	3 (3.2)	0 (0.6)	0 (0.1)
.80	.78	59 (66.7)	29 (22.2)	8 (7.4)	2 (2.5)	2 (1.2)
.78	.75	54 (63.9)	32 (23.1)	10 (8.3)	3 (3.0)	1 (1.7)
.77	.76	56 (62.6)	31 (23.4)	9 (8.8)	2 (3.3)	2 (1.9)
.61	.59	29 (43.9)	33 (24.6)	19 (13.8)	10 (7.8)	9 (9.9)
.60	.51	25 (42.9)	30 (24.5)	18 (14.0)	10 (8.0)	17 (10.6)
.52	.52	21 (35.1)	29 (22.8)	22 (14.8)	13 (9.6)	15 (17.7)
.47	.46	14 (30.7)	24 (21.3)	21 (14.7)	15 (10.2)	26 (23.1)
.28	.28	3 (16.3)	8 (14.6)	13 (11.4)	8 (9.6)	68 (48.1)

^a Values in parentheses are obtained from a computer program for calculating random sorting of the mono (RS-) and difunctional (-S-) groups into molecules on the basis of equal probability of all S-S bonds.

TABLE III

MOLE PERCENTAGE OF VARIOUS MOLECULES FOUND AT EQUILIBRIUM IN MIXTURES OF DI-*t*-BUTYL DISULFIDE WITH SULFUR AT 120°

$-R = (\text{CH}_3)_3\text{C}/\text{S}-$											$(\text{CH}_3)_3\text{C}-\text{S}_n\text{C}(\text{CH}_3)_3$ for $n \geq 11$
From ingredients	From n.m.r. data	$(\text{CH}_3)_3\text{C}-\text{S}_2\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_3\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_4\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_5\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_6\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_7\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_8\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_9\text{C}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{C}-\text{S}_{10}\text{C}(\text{CH}_3)_3$	$n \geq 11$
0.87	0.83	77 (77.1)	14 (17.7)	5 (4.1)	2 (0.9)	1 (0.2)	1 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
.52	.52	49 (35.1)	10 (22.8)	15 (14.8)	8 (9.6)	6 (6.2)	4 (4.0)	3 (2.6)	2 (1.7)	1 (1.1)	2 (2.1)
.49	.46	39 (32.5)	12 (21.9)	17 (14.8)	11 (10.0)	6 (6.8)	3 (4.6)	4 (3.1)	2 (2.1)	2 (1.4)	4 (2.8)
.48	.45	43 (31.6)	9 (21.6)	15 (14.8)	8 (10.1)	7 (6.9)	5 (4.7)	4 (3.2)	2 (2.2)	1 (1.5)	6 (3.4)
.32	.32	13 (19.1)	13 (15.4)	17 (12.5)	12 (10.1)	10 (8.2)	11 (6.6)	7 (5.3)	4 (4.3)	3 (3.5)	10 (15.0)

respect to the sorting of end, RS-, and middle, -S-, groups of fixed functionality was achieved. The experimental data corresponding to equilibria in the system involving methyl-terminated chains are presented in Table II and in the system involving *t*-butyl terminated chains in Table III. In these tables, the experimental data are compared with the statistical values calculated for the same composition on the basis of random sorting^{11,12} of the end and middle groups with no rings present. Material-balance calculations show that, within experimental error (*ca.* 5% of the total sulfur), there are no rings in the methyl polysulfide system for $R > ca.$ 0.75 and in the *t*-butyl system for any composition studied. This means that just a small proportion of end groups need be added to a system of sulfur rings to convert all rings to chains at equilibrium. In other words, the S₈ rings are in equilibrium in significant amounts only with the extremely long alkyl-terminated sulfur chains at 120°. In contrast, substantial amounts of crystalline S₈ precipitate at room temperature (see Experimental section) owing to the action of Le Chatelier's principle.

In the methyl- and probably in the *t*-butyl-terminated systems, the disulfide molecules are present at equilibrium in smaller amounts than predicted by random sorting of the RS- and -S- groups. Likewise, the trisulfide molecules seem to be present in excess—a phenomenon having the same underlying cause as their early formation in the kinetic runs. These effects are attributable to changes in the energy of a sulfur atom in a chain due to replacement of a sulfur by a carbon atom at a point one or two atoms removed down the chain.¹²

Condensation Polymerizations to Form Alkyl Sulfides

(11) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1942); **12**, 125 (1944); P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2718 (1952).

(12) The theory of this effect will be published shortly by L. C. D. Groeneweghe, D. W. Matula, and J. R. Van Wazer.

or Selenides Plus Methyl Chloride.—It is found that, without application of heat, mixtures of dimethyl with dichloro sulfides or selenides undergo elimination of methyl chloride to form S-S or Se-Se bonds, respectively. With mixtures of $(\text{CH}_3)_2\text{S} + \text{SeCl}_2$, $(\text{CH}_3)_2\text{Se} + \text{Se}_2\text{Cl}_2$, and $(\text{CH}_3)_2\text{Se}_2 + \text{Se}_2\text{Cl}_2$, the bulk of the methyl chloride is eliminated in the first few minutes during the initial exothermic reaction. Initial formation of a complex introduces a complication into the sequence of reactions in mixtures of $(\text{CH}_3)_2\text{S}_2 + \text{SCl}_2$. Along with the condensation polymerization, scrambling of methyl groups with chlorine atoms is always observed. In the sulfur-based systems, the data show that the scrambling occurs through making and breaking of S-S or S-Cl bonds, with the S-C bonds always remaining intact unless the mixture is strongly heated for a long period of time. The same situation is considered to hold in the selenium-based systems, except that the temperatures for measurably rapid breaking of Se-C bonds are lower (but still in the range above 150°) than for breaking S-C bonds.

As expected, the proportion of total molecules appearing in the form of long-chain species is greatest when there were equimolar amounts of methyl groups and chlorine atoms in the reagent mixture. Because of the small amount of residual methyl groups and the solvent action of the excess dichloro-terminated chains, unusually clear n.m.r. spectra are obtained when the chlorine/methyl ratio in the reagent mixture is larger than unity. On the other hand, for this ratio smaller than unity, the n.m.r. spectra are rather crowded (and hence may be analyzed only with difficulty to give precise quantitative data) so that this region of composition gives the most detailed but least accurate information.

Typical rate curves for a small and large excess of sulfur dichloride in reaction mixtures of $(\text{CH}_3)_2\text{S} + \text{SCl}_2$ are presented in Fig. 3 and 4. In these figures,

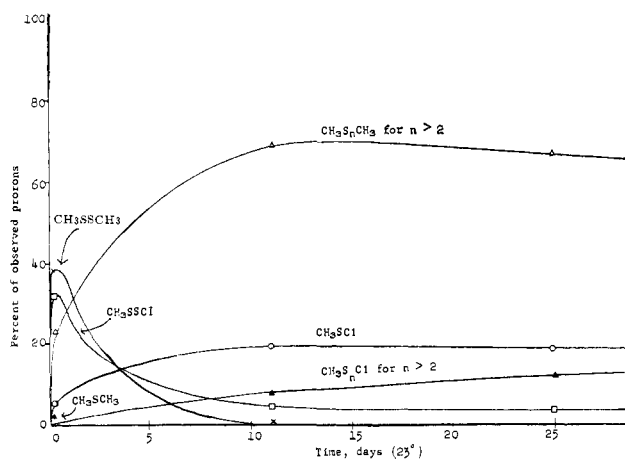


Fig. 3.—Condensation polymerization (with no heat applied) of a mixture of dimethyl sulfide and sulfur dichloride exhibiting an initial mole ratio of chlorine/methyl = 1.35.

the chains (terminated with methyl groups on either one or both ends) which are larger than the disulfide are lumped together for the sake of clarity. With a relatively small excess of sulfur dichloride as in Fig. 3, the amount of the chains longer than the disulfide, having methyl groups on both ends, maximizes in a shorter time than does the amount of same sized chains terminated with one methyl group and one chlorine atom.¹³ This shows that in the early parts of the reaction, the rate of polymerization is faster than the effective rate of scrambling. However, the number of all chains longer than the disulfide finally diminishes to the more-or-less small value corresponding to the dynamic equilibrium between variously sized chains. As the total proportion of SCl_2 to $(\text{CH}_3)_2\text{S}$ in the reagent mixture is greatly increased, as in the example of Fig. 4, the proton n.m.r. data (which, of course, show the methyl groups only) are then necessarily concerned with only a small part of the over-all set of reactions so that the observed rate curves become superficially more simple (compare Fig. 4 with Fig. 3).

When equal amounts of methyl groups and chlorine atoms are present in the starting mixture of dimethyl sulfide and sulfur dichloride, the main kinetic process is production of long chains so that in about 7 days at room temperature the liquid is converted to a solid consisting of a gelatinous mixture of long-chain compounds mixed with crystalline sulfur (S_8 rings); and the rate of further reaction is then greatly reduced due to the onset of diffusion control.¹⁴ From all of the kinetic data on various mixtures of dimethyl sulfide with sulfur dichloride, we conclude that condensation polymerization occurs more rapidly than scrambling which, in turn, is considerably faster than the equilibration rate processes whereby S_8 rings are formed. The complex formed upon mixing dimethyl disulfide with sulfur dichloride is soluble and shows up in the n.m.r. spectrum. When the chlorine/methyl ratio in this mixture is large, the process of condensation polymerization subsequent to the complex formation begins promptly; but, when this ratio is small, polymerization does not show up for

(13) For data on the chain compounds terminated at both ends with chlorine atoms, see F. Fehér, K. Naused, and H. Weber, *Z. anorg. allgem. Chem.*, **290**, 303 (1957).

(14) *I.e.*, this system does not show the Norrish-Trommsdorff effect; see P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 124-129; and G. V. Schultz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

several days. Another communication is being prepared concerning the complex.

In addition to a small amount of finely divided black precipitate (elemental selenium) formed immediately upon mixing, a similar but more rapid set of reactions involving scrambling of methyl groups with chlorine atoms as well as condensation polymerization (all readily followed by n.m.r. spectroscopy) is found for mixtures of dimethyl selenide or dimethyl diselenide with dichloro diselenide. Concomitant with the reactions observed in solution, there is a slow but steady precipitation of clear, colorless crystals, which we have attributed to the ionic species $[(\text{CH}_3)_3\text{Se}]^+\text{Cl}^-$. After longer periods of time, precipitation of either the red or the gray form of elemental selenium is observed under conditions similar to those reported below.

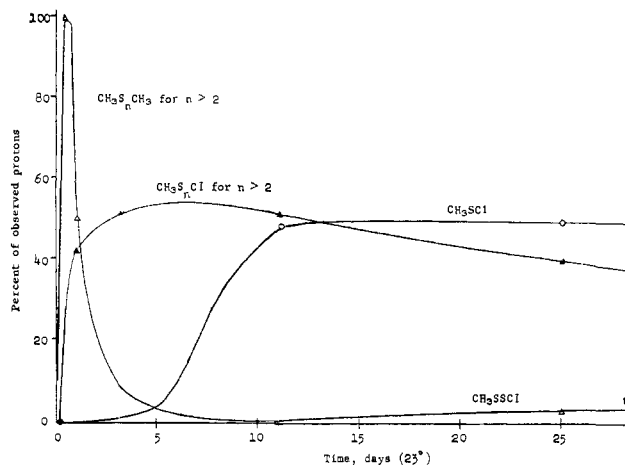


Fig. 4.—Condensation polymerization (with no heat applied) of a mixture of dimethyl sulfide and sulfur dichloride exhibiting an initial mole ratio of chlorine/methyl = 31.

In the interaction of dimethyl diselenide with dichloro diselenide, these colorless crystals were not formed so that the reactions occurring in solution could be more easily followed quantitatively. In this system, the first more-condensed species than the diselenide to appear in the proton n.m.r. spectra is the mixed tetraselenide, $\text{CH}_3\text{Se}_4\text{Cl}$. Then there is the usual sequence of continuing condensation plus scrambling until the larger chains reorganize to give elemental selenium, leaving the monofunctional terminal substituents (with a selenium atom still attached to the methyl) in shorter-chain molecules. In the range of equimolar proportions of the reagents, the precipitate is found to be gray selenium, otherwise known as metallic selenium, which has been shown¹⁵ to consist of long spiralled chains. For ratios of the starting reagents quite far from the equimolar mixture, the onset of precipitation is slower (3-7 days), and the precipitate is composed of red, carbon disulfide-soluble selenium, which has been shown¹⁶ to exhibit an Se_8 ring structure.

Condensation Polymerizations Involving Dialkyl Sulfides Other Than $(\text{CH}_3)_2\text{S}$.—The reactions of di-*t*-butyl disulfide or dibenzyl disulfide with sulfur dichloride proceed through the normal stages of concomitant scrambling and condensation polymerization, without the formation of a complex as found in the reaction involving dimethyl disulfide. The majority of the *t*-

(15) E. Grison, *J. Chem. Phys.*, **19**, 1109 (1951); M. Straumanis, *Z. Krist.*, **102**, 432 (1940).

(16) R. D. Burbank, *Acta Cryst.*, **4**, 140 (1951), and R. E. Marsh, L. Pauling, and J. D. McCullough, *ibid.*, **6**, 71 (1953).

butyl chloride is volatilized in the first few minutes of reaction, as with methyl chloride. However, benzyl chloride does not volatilize under the usual conditions of reaction with no application of heat but is seen from the n.m.r. spectrum to increase steadily in the reaction mixture. This shows that the condensation reaction is not driven forward by elimination of a volatile product but that formation of the alkyl chloride is thermodynamically favorable.

Reactions of Dimethyl Sulfide with Sulfur.—At temperatures below the transition (*ca.* 168°) of elemental sulfur from S_8 rings to long chains, there was no observable reaction between dimethyl sulfide and elemental sulfur held in sealed tubes over a period of several months. At higher temperatures, some reaction was observed. Thus, after 2.5 months at 190°, the mixtures were all straw to reddish colored liquids with considerable gas pressure but no solids. Upon opening the tubes, the odors of hydrogen sulfide and methyl mercaptan were very noticeable; n.m.r. study of the liquids removed from the tubes showed that only a small proportion of the reagents had undergone reaction. The n.m.r. spectra showed the presence of sulfides terminated by methyl groups and/or hydrogen atoms, as well as a group of resonance peaks in the spectral region corresponding to a methylene group with two sulfurs bonded to it. These were attributed to structures¹⁷ based on $-\text{CH}_2-\text{C}-$ chains stemming from a reaction between sulfur and the methyl groups to give H_2S plus sulfur substitution of a methyl hydrogen.

(17) Such compounds prepared by a very different procedure have been described by F. Feher and K. Vogelbruch, *Chem. Ber.*, **91**, 996 (1958).

Discussion

The n.m.r. evidence for the existence of variously sized sulfur and selenium chain molecules *terminated with different groups at either end* opens a new vista for preparative chemists in the sulfur area. As far as we know, the previously described sulfur-based molecules having two different terminating groups are restricted to the monosulfur compounds.² Also of interest are our kinetic data which show that, in the absence of catalysts, the polysulfides may be kept at room temperature with inappreciable rearrangement for many months. The observation concerning precipitation of gray *vs.* red selenium may prove capable of development as a preparative method for the different allotropic forms of this element.

The attainment of a dynamic equilibrium between the variously sized dimethyl polysulfides is thought to occur because of the good stability of the C-S bond. Presumably the thermodynamic equilibrium corresponding to an infinite time for equilibration in the case of the family of dimethyl polysulfides would be simply a mixture of dimethyl monosulfide with elementary sulfur similar to the case of the hydrogen-terminated sulfur chains, as calculated from the available thermodynamic data.¹⁸

Acknowledgments.—We wish to thank Messrs. A. Y. Coran and C. D. Trivette for a stimulating discussion when the work reported herein was about half finished. We are also indebted to Mr. C. H. Dungan for carrying out many of the calculations on which the figures and tabulations are based.

(18) F. Feher and J. Winkhaue, *Z. anorg. allgem. Chem.*, **292**, 210 (1957).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

Some Transition Metal Complexes of Substituted Thioureas. II. Nickel(II)^{1a}

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The preparation and properties of the crystalline compounds $[\text{Ni}(\text{naptu})_4\text{Cl}_2]$ ($\text{naptu} = 1-(1\text{-naphthyl})\text{-2-thiourea}$), $[\text{Ni}(\text{naptu})_2\text{X}_2]$ ($\text{X} = \text{Br}$ or I), $[\text{Ni}(\text{etu})_4\text{X}_2]$ ($\text{X} = \text{Cl}$, Br , I , ClO_4 , or NO_3 ; $\text{etu} = \text{ethylenethiourea}$), and $[\text{Ni}(\text{etu})_6](\text{ClO}_4)_2$ are described. The chloro and bromo etu complexes exist in both yellow and orange forms which are considered to be geometric isomers of octahedral nickel. $[\text{Ni}(\text{naptu})_4\text{Cl}_2]$ and $[\text{Ni}(\text{etu})_6](\text{ClO}_4)_2$ are octahedral, while $[\text{Ni}(\text{naptu})_2\text{Br}_2]$ and $[\text{Ni}(\text{naptu})_2\text{I}_2]$ are tetrahedral. The iodo etu complex is shown to be six-coordinate though diamagnetic. The compound $[\text{Ni}(\text{etu})_4](\text{ClO}_4)_2$ is square-planar as is crystalline $[\text{Ni}(\text{etu})_4](\text{NO}_3)_2$. In solution, however, all of the compounds lose ligand and retain coordinated anion. Assignment of stereochemistry is made in conjunction with spectral, magnetic, electrochemical, molecular weight, and X-ray powder data.

Systems in which nickel(II) attains a variety of stereochemical environments when coordinated to one primary donor are rare.² Discovery of such a system, however, gives us the opportunity of studying any one principal donor in a variety of configurations and thereby elucidating the factors which determine the stereochemistry attained by nickel. The study of such a series of compounds in which sulfur is the primary donor atom forms the basis of this report.

We report here octahedral, paramagnetic and diamagnetic tetragonal, square-planar, and tetrahedral

complexes of nickel, as well as what appear to be the first isolated isomers of octahedral nickel. The factors which govern the adoption of a particular structure by nickel are also explored.

Experimental³

Reagents.—Nickel nitrate, perchlorate, and chloride were reagent grade and were used without further purification. Nickel bromide and iodide were prepared from nickel carbonate and the corresponding halo acid. Ethylenethiourea was obtained from K and K Chemical and was purified by recrystallization from ethanol. Naphthylthiourea was obtained from Eastman and was purified by recrystallization from 2-propanol.

Dichlorotetrakis(ethylenethiourea)nickel(II). Yellow Complex.— $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (14 g.) was dissolved in 75 ml. of absolute ethanol and was added to a hot solution of 4 g. of ethylenethiourea in ethanol. Cooling afforded yellow crystals of the compound.

(1) (a) Part I: R. L. Carlin and S. L. Holt, Jr., *Inorg. Chem.*, **2**, 849 (1963); (b) further details will be found in the thesis of S. L. Holt, Jr., Brown University, June, 1965.

(2) D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

(3) Microanalyses by Schwarzkopf Microanalytical Laboratory.