Polysulfide Exchange Reactions. I. Kinetics and Mechanism of the Thermal Exchange between Diethyl Trisulfide and Di-*n*-propyl Trisulfide

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Kinetic parameters were determined for the reversible reaction between diethyl and di-*n*-propyl trisulfide. A free-radical chain mechanism, which accounts for the exchange reaction and also for the slower disproportionation to di- and tetrasulfides, is proposed. The over-all activation energy is about 29 kcal./mole but decreases with tetrasulfide formation.

The ultraviolet light or base-catalyzed exchange between di- and higher polysulfides is well documented.[1]

$$R_1SSR_1 + R_2SSR_2 \longrightarrow 2R_1SSR_2$$

Haraldson, *et al.*,[1b] in agreement with McAllan, *et al.*,[1c] found that the equilibrium constant for the exchange between simple unhindered alkyl disulfides is close to 4, indicating nearly statistical distribution of products. Westlake, Laquer, and Smyth[2] observed that diethyl disulfide and sulfur in the presence of dibutylamine give diethyl trisulfide. Exchange reactions between diethyl tetrasulfide and radioactive diethyl trisulfide (EtSS*SEt), between diethyl disulfide and radioactive diethyl trisulfide, and between radioactive sulfur and diethyl disulfide were examined by Guryanova and coworkers.[3] The catalytic effect of various amines on the exchange between diethyl and dibenzyl trisulfides was also studied.[3d] These authors observed that only the central sulfur atoms were exchangeable in these systems; no carbon-to-sulfur bonds were broken.

The reversible polymerization of S_8 at temperatures not far removed from those used for vulcanization[4] and stress relaxation of polysulfide polymers *via* exchange of polysulfidic links[5] are processes which suggest that polysulfide exchange reactions may be involved in the vulcanization process itself. A kinetic study of the exchange between diethyl trisulfide and di-*n*-propyl trisulfide was undertaken with the hope of shedding some light on the mechanism by which such exchanges can occur.

The variation of diethyl trisulfide and di-*n*-propyl trisulfide concentrations with time over the temperature range 132–148° is shown in Table I. The major product is ethyl *n*-propyl trisulfide. After long reaction times, equilibration of the three trisulfide concentrations is approached. After very long reaction periods, di- and tetrasulfide disproportionation products appear in substantial amounts. Over the reaction period of primary interest in this paper, the over-all reaction is

$$EtS_3Et + PrS_3Pr \rightleftharpoons 2EtS_3Pr$$

The equilibrium constant K is

$$K = [EtS_3Pr]^2/[EtS_3Et][PrS_3Pr]$$

Within experimental error, a statistical distribution of products is obtained; that is, $K = 4$. This value is not unexpected, as a result of the work of Haraldson, *et al.*,[1b] who found an equilibrium constant of 5.6 for the ultraviolet light or base-catalyzed exchange between dimethyl and diethyl disulfides.

The rate of exchange was increased in the presence of diethyl tetrasulfide. Data for the disappearance of diethyl and di-*n*-propyl trisulfide concentrations with time are tabulated in Table II. The diethyl trisulfide used in these runs contained 0.3% diethyl tetrasulfide. The data in Table II fits a first-order reversible rate equation (eq. 1), with only a hint of curvature in the direction of increasing exchange rate with reaction time. The rate constants k_a' calculated from the data in Table II are listed in Table III. The activation energy E_a' for the exchange is 26.3 ± 0.9 kcal./mole. The Arrhenius equation is $k_a' = 9.1 \times 10^9 e^{-26,300/RT}$.

$$\ln \frac{A - A_e}{A_0 - A_e} = -k_a t \qquad (1)$$

Figure 1 shows a plot according to eq. 1 of the data obtained for the exchange using pure trisulfides (Table I). The curvature here is quite distinct. A logical explanation for the curvature is that the exchange rate increases owing to catalysis by the small quantities of tetrasulfide formed during the exchange. The curvature problem can be circumvented (at the expense of precision) by comparing slopes of the individual rate plots at equal degrees of conversion. The rate constants k_a determined from the slopes of the reaction curves (Figure 1) at 18, 33, and 55% reaction, corresponding to values of $\ln (A_0 - A_e)/(A - A_e)$ of 0.2, 0.4 and 0.6, are given in Table IV. The related activation energies E_a are 29.0, 28.6, and 28.2 ± 2.0 kcal./mole at values of $\ln (A_0 - A_e)/(A - A_e)$ of 0.2, 0.4, and 0.6, respectively. The Arrhenius equation for the 29.0-kcal. line is $k_a = 1.3 \times 10^{11} e^{-29,000/RT}$.

The lack of influence of the solvent nitrobenzene (Table III) on the exchange rate provides strong support for a free-radical mechanism. The reaction then would proceed through homolytic dissociation of a trisulfide molecule to give two thiyl radicals (eq. 2).

$$RSSSR \longrightarrow RS\cdot + \cdot SSR \qquad (2)$$

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(1) (a) S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Petroleum*, **39**, 206 (1953); (b) L. Haraldson, C. J. Olander, S. Sunner, and E. Varde, *Acta Chem. Scand.*, **14**, 1509 (1960); (c) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

(2) H. E. Westlake, Jr., H. L. Lacquer, and C. P. Smyth, *ibid.*, **72**, 436 (1950).

(3) (a) E. N. Guryanova, Y. K. Syrkin, and L. S. Kuzina, *Dokl. Akad. Nauk SSSR*, **86**, 107 (1952); *Chem. Abstr.*, **47**, 1475*f* (1953); (b) E. N. Guryanova and V. N. Vasileva, *Zh. Fiz. Khim.*, **28**, 60 (1954); *Chem. Abstr.*, **48**, 11888*a* (1954); (c) E. N. Guryanova, Y. K. Syrkin, and L. S. Kuzina, *Dokl. Akad. Nauk SSSR*, **85**, 1021 (1952); *Chem. Abstr.*, **47**, 5877*e* (1953); (d) E. N. Guryanova and L. A. Egorova, *Zh. Obshch. Khim.*, **28**, 1745 (1958); *Chem. Abstr.*, **53**, 1108*d* (1959).

(4) (a) R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943); (b) F. Fairbrother, G. Gee, and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955); (c) A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959).

(5) M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).

TABLE I

DISAPPEARANCE OF TETRASULFIDE-FREE DIETHYL AND DI-*n*-PROPYL TRISULFIDES[a]

t, sec. × 10^{-3}	$[EtS_3Et]$[b]	$[PrS_3Pr]$[b]
	At 131.95°	
0	0.1003	0.1000
1.74	0.0994	0.0982
3.66	0.0962	0.0989
5.40	0.0947	0.0998
7.20	0.0928	0.0989
10.92	0.0877	0.0950
14.40	0.0839	0.0903
18.00	0.0787	0.0861
21.78	0.0763	0.0829
29.10	0.0682	0.0750
	At 140.0°	
0	0.0501	0.0500
0.90	0.0499	0.0499
1.80	0.0499	0.0492
2.70	0.0480	0.0485
3.60	0.0463	0.0468
5.40	0.0458	0.0455
7.20	0.0440	0.0442
9.00	0.0431	0.0430
10.98	0.0410	0.0408
14.52	0.0380	0.0379
	At 140.0°	
0	0.1003	0.1000
0.90	0.0990	0.1006
1.80	0.0962	0.0984
2.70	0.0939	0.0959
3.60	0.0931	0.0951
5.52	0.0874	0.0898
7.38	0.0817	0.0838
9.00	0.0779	0.0801
10.80	0.0736	0.0756
14.52	0.0683	0.0705
	At 140.0°	
0	0.2006	0.2000
1.80	0.1880	0.1872
2.70	0.1809	0.1782
3.60	0.1754	0.1735
5.40	0.1626	0.1613
7.32	0.1504	0.1499
9.06	0.1438	0.1435
10.80	0.1345	0.1336
14.40	0.1250	0.1240
	At 147.95°	
0	0.1003	0.1000
0.90	0.0977	0.0987
1.80	0.0938	0.0946
2.70	0.0884	0.0908
3.60	0.0832	0.0858
5.82	0.0741	0.0765
7.20	0.0698	0.0713
9.00	0.0636	0.0654
10.80	0.0608	0.0620
14.40	0.0544	0.0546

[a] Prepared by method B, Experimental Section. [b] Moles per liter.

TABLE II

RATES OF DISAPPEARANCE OF DIETHYL AND DI-*n*-PROPYL TRISULFIDES[a] AT VARIOUS TEMPERATURES

t, sec. × 10^{-3}	$[EtS_3Et]$	$[PrS_3Pr]$
	At 130.0°	
0	0.1003	0.1006
3.60	0.0878	0.0918
7.20	0.819	0.0837
10.80	0.0748	0.0782
14.40	0.0699	0.0722
21.72	0.0622	0.0650
28.80	0.0573	0.0600
	At 134.9°	
0	0.1003	0.1006
2.82	0.0892	0.0907
5.40	0.0845	0.0850
8.22	0.0736	0.0753
10.80	0.0682	0.0713
12.60	0.0648	0.0672
16.20	0.0597	0.0619
21.60	0.0558	0.0571
	At 140.0°	
0	0.1003	0.1006
1.80	0.0897	0.0897
3.60	0.0785	0.0808
7.20	0.0675	0.0696
10.80	0.0597	0.0621
14.90	0.0550	0.0575
21.60	0.0503	0.0534
	At 140.1°[b]	
0	0.0996	0.0998
1.80	*c*	0.0876
3.66	*c*	0.0802
7.20	*c*	0.0672
10.80	*c*	0.0593
14.58	*c*	0.0547
	At 140.0°[d]	
0	0.1019	0.1020
3.72	0.0813	0.0825
7.20	0.0707	0.0712
10.80	0.0604	0.0616
	At 144.3°	
0	0.1003	0.1006
1.20	0.0895	0.0912
2.40	0.0814	0.0826
3.60	0.0742	0.0767
5.40	0.0661	0.0688
7.20	0.0602	0.0631
10.80	0.0533	0.0565
	At 150.15°	
0	0.1003	0.1006
0.90	0.0886	0.0890
1.80	0.0813	0.0797
2.70	0.0731	0.0736
3.60	0.0662	0.0684
5.40	0.0579	0.0604
7.20	0.0547	0.0562

[a] Prepared by method A; see Experimental Section for analysis. Diethyl trisulfide contained 0.3% diethyl tetrasulfide. [b] Solvent 60:40 benzene–nitrobenzene. [c] Not measurable owing to $PhNO_2$ interference. [d] Reaction carried out under nitrogen.

Allen[6] has reported a value of 60.61 kcal./mole for the thermochemical bond strength of the S–S bond in hydrogen trisulfide. A similar value for the S–S bond in diethyl or di-*n*-propyl trisulfide would be expected. Since the activation energy for the trisulfide exchange is 29 kcal./mole, a chain reaction must be involved.

Gee and co-workers,[4b] Gardner and Fraenkel,[7] and Tobolsky and Eisenberg[4c] have examined the

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[6] T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).

[7] D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

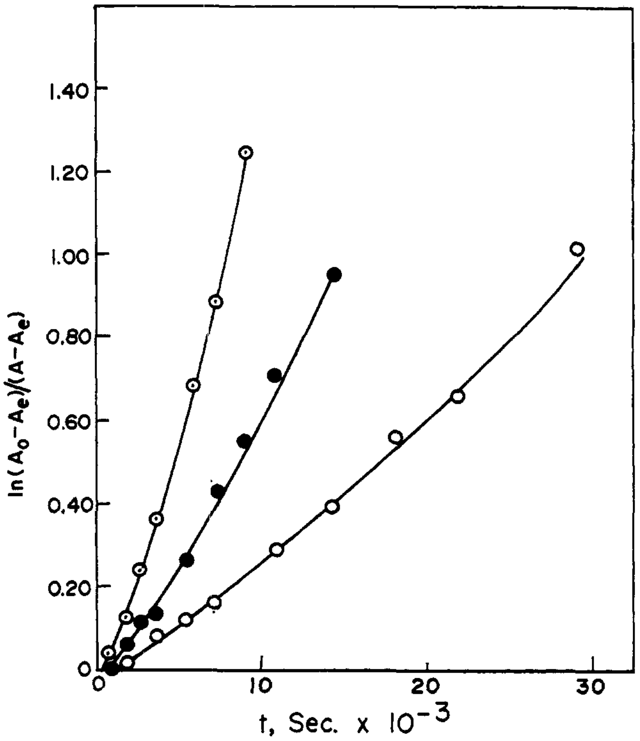

Figure 1.—Effect of temperature on rate of disappearance of tetrasulfide-free diethyl and di-*n*-propyl trisulfides: ⊙, 147.95°; ●, 140.0°; and ○, 131.95°.

TABLE III

RATE CONSTANTS CALCULATED FROM TABLE II ACCORDING TO EQ. 1

Reaction Temp., °C.	$[EtS_3Et]_0$[a]	$[PrS_3Pr]_0$	$k_a' \times 10^5$, sec.$^{-1}$
130.0	0.1003	0.1006	6.3
134.9	0.1003	0.1006	9.1
140.0	0.1003	0.1006	14.0
140.1[b]	0.0996	0.0998	15.0
140.0[c]	0.1019	0.1020	14.0
144.3	0.1003	0.1006	20.0
150.15	0.1003	0.1006	30.0

[a] Contained 0.3% of diethyl tetrasulfide. [b] Solvent, 60:40 (v./v.) benzene–nitrobenzene. [c] Under nitrogen.

TABLE IV

VALUES OF k_a AT VARIOUS TEMPERATURES FOR DIFFERENT DEGREES OF CONVERSION

Reaction Temp., °C.	$k_a \times 10^5$, sec^{-1} — $\ln(A_0 - A_e)/(A - A_e)$ 0.2	0.4	0.6
131.95	3.1	3.5	3.9
140.0	6.4	7.3	7.6
147.95	12.1	13.3	14.8

thermal polymerization of S_8 in detail. In addition to the polymerization, which is initiated by a sulfur diradical produced by homolytic dissociation of S_8, a rapid exchange occurs between the linear polythiyl radicals and the linear polysulfides present. Gardner and Fraenkel obtained a value of 3.1 kcal./mole for the activation energy of this exchange. By analogy, in

$$\mathrm{{\sim}S\cdot + {\sim}S{-}S{\sim} \longrightarrow {\sim}S{-}S{\sim} + \cdot S{\sim}}$$

the trisulfide exchange an ethyl or *n*-propyl mono- or dithiyl radical should react rapidly with a trisulfide molecule.

$$\mathrm{R_1S\cdot + R_2SSSR_2 \longrightarrow R_1SSSR_2 + R_2S\cdot} \tag{3}$$

$$\mathrm{R_1SS\cdot + R_2SSSR_2 \longrightarrow R_1SSSSR_2 + R_2S\cdot} \tag{4}$$

The fact that molecular oxygen has no effect on a reaction which from all other indications proceeds through free-radical intermediates is at first glance disturbing. However, by analogy with the polythiyl radical exchange reaction in polymeric sulfur, with an activation energy of 3.1 kcal./mole, the energy for exchange of a thiyl radical with trisulfide should be low. It appears that the activation energy is indeed low enough for the trisulfide to compete favorably with molecular oxygen for the thiyl radicals.

To account for the single product of the exchange, namely mixed trisulfide, attack of a thiyl radical must occur exclusively on the central trisulfide sulfur atom (eq. 2 and 3). If displacement took place on an α-sulfur atom, the products would be disulfide and tetrasulfide. Examination of molecular models indicates that there may be a small steric contribution at the α-sulfur atoms. However, the difference in reactivities of the two types of sulfur atoms in the trisulfide molecule must be due primarily to electronic effects. Spectral studies[8] generally show that divalent sulfur is electron withdrawing. In addition, alkyl groups are electron releasing in nature. The central sulfur atom of an alkyl trisulfide molecule should thus be electron rich, therefore more susceptible to attack by a thiyl radical.

Examination of eq. 3 and 4 shows that either radical from the initiation step (eq. 2) gives rise to a monothiyl radical chain carrier. If the kinetic chain length is long, differentiation between mono- and dithiyl radicals can be neglected in the kinetic treatment. The termination step then consists of bimolecular combination of two monothiyl radicals to form a molecule of disulfide. Thus, the *initiation and termination steps constitute disproportionation of trisulfide to disulfide and tetrasulfide*, and the slow formation of disulfides and tetrasulfides is accounted for. If the chain length

$$\mathrm{2RS_3R \longrightarrow RS_2R + RS_4R}$$

is long, the disproportionation reaction will be minor, allowing the approximation that the total trisulfide concentration is constant throughout the reaction.

The following reaction scheme may then be written, if one assumes that the individual rates of initiation, propagation, and termination are identical. Let A = EtS_3Et, B = PrS_3Pr, C = EtS_3Pr, R_1 = $EtS\cdot$, and R_2 = $PrS\cdot$. Then

$$\left.\begin{array}{l} \mathrm{A \longrightarrow 2R_1} \\ \mathrm{B \longrightarrow 2R_2} \\ \mathrm{C \longrightarrow R_1 + R_2} \end{array}\right\} \text{initiation, rate } k_{i3}$$

$$\left.\begin{array}{l} \mathrm{R_1 + B \longrightarrow R_2 + C} \\ \mathrm{R_2 + A \longrightarrow R_1 + C} \\ \left\{\begin{array}{l} \mathrm{R_1 + C \longrightarrow R_2 + A} \\ \mathrm{R_1 + C \longrightarrow R_1 + C} \end{array}\right. \\ \left\{\begin{array}{l} \mathrm{R_2 + C \longrightarrow R_1 + B} \\ \mathrm{R_2 + C \longrightarrow R_2 + C} \end{array}\right. \end{array}\right\} \text{propagation, rate } k_p \tag{5}$$

$$\left.\begin{array}{l} \mathrm{2R_1} \xrightarrow{k_t} \\ \mathrm{2R_2} \xrightarrow{k_t} \text{termination products} \\ \mathrm{R_1 + R_2} \xrightarrow{2k_t} \end{array}\right\} \text{termination}$$

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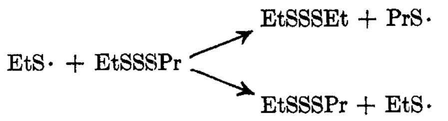
[8] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, 1962, p. 31 ff.

Analysis of the propagation steps (eq. 5) reveals that reaction of R_1 with C does not necessarily lead to a new product (eq. 6). To simplify derivation of the integrated rate equation, the assumption will be made that the probability of obtaining a new product is one-half; that is, the electronic and steric differences of the ethyl and n-propyl groups will be neglected. The approximation is reasonable in light of the experimentally observed statistical product distribution. These same considerations hold for reaction of R_2 with C.



$$\mathrm{EtS\cdot + EtSSSPr} \begin{array}{l} \nearrow \mathrm{EtSSSEt + PrS\cdot} \\ \searrow \mathrm{EtSSSPr + EtS\cdot} \end{array} \qquad (6)$$

Steady-state kinetic treatment gives the expressions 7 and 8. Addition of eq. 7 and 8, followed by rearrangement, gives eq. 9 where $C_t = [A] + [B] + [C] =$ total trisulfide concentration, which is essentially constant since the disproportionation reaction is slow.

$$\mathrm{d}[R_1]/\mathrm{d}t = 2k_{i3}[A] + k_{i3}[C] + k_pR_2[A] + 0.5k_p[R_2][C] - k_p[R_1][B] - 0.5k_p[R_1][C] - 2k_t[R_1] - 2k_t[R_1][R_2] = 0 \quad (7)$$

$$\mathrm{d}[R_2]/\mathrm{d}t = 2k_{i3}[B] + k_{i3}[C] + k_p[R_1][B] + 0.5k_p[R_1][C] - k_p[R_2][A] - 0.5k_p[R_2][C] - 2k_t[R_2] - 2k_t[R_1][R_2] = 0 \quad (8)$$

$$([R_1] + [R_2])^2 = k_{i3}C_t/k_t \quad (9)$$

For equimolar initial concentrations of A and B, the radical concentrations of R_1 and R_2 are equal if the approximation that the individual rates of initiation, propagation, and termination are the same is valid. Thus

$$[R_1] = [R_2] = R_t/2 \quad (10)$$

and, from eq. 9

$$R_t = (k_{i3}C_t)^{1/2}/k_t^{1/2} \quad (11)$$

The rate of disappearance of A is given by eq. 12.

$$-d[A]/\mathrm{d}t = k_{i3}[A] + k_p[R_2][A] - 0.5k_p[R_1][C] \quad (12)$$

Substitution for $[R_1]$ and $[R_2]$ from eq. 10, and for [C] according to the relationship $[C] = 2([A]_0 - [A])$, gives eq. 13, which upon integration becomes

$$-d[A]/\{[A](k_{i3} + k_p[R_t] - 0.5k_p[R_t][A_0])\} = \mathrm{d}t \quad (13)$$

$$\ln\{[A](k_{i3} + k_pR_t) - 0.5k_pR_t[A]_0/[A]_0(k_{i3} + k_pR_t) - 0.5k_pR_t[A]_0\} = -(k_{i3} + k_pR_t)t \quad (14)$$

At equilibrium, $\mathrm{d}[A]/\mathrm{d}t = 0$; hence, the equilibrium concentration $[A]_e$, obtained by setting eq. 13 equal to zero, is

$$[A]_e = 0.5k_pR_t[A]_0/(k_{i3} + k_pR_t) \quad (15)$$

Upon substitution of eq. 11 and 15 into eq. 14, we obtain eq. 16. The kinetic chain length will be defined as the rate of propagation divided by the rate of initiation. The rate of propagation is

$$\ln([A] - [A]_e)/([A]_0 - [A]_e) = k_{i3}[1 + k_pC_t^{1/2}/(k_{i3}k_t)^{1/2}]t \quad (16)$$

$$r_p = k_p[R_1][B] + k_p[R_2][A] + 0.5k_p[R_1][C] + 0.5k_p[R_2][C] \quad (17)$$

Substitution for $[R_1]$ and $[R_2]$ from eq. 10 gives

$$r_p = 0.5k_pR_tC_t \quad (18)$$

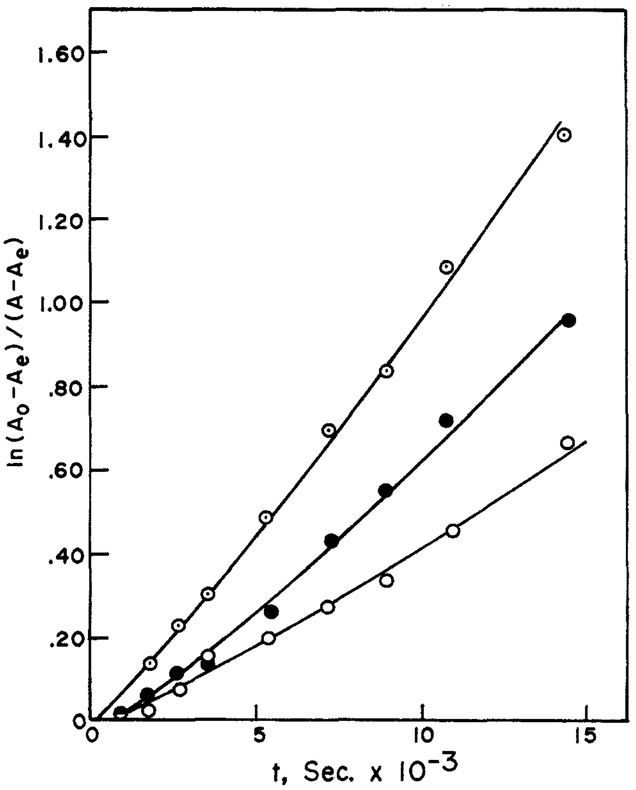


Figure 2.—Effect of initial symmetrical trisulfide concentrations on exchange rate at 140.0°: ○, $[EtS_3Et]_0 = [PrS_3Pr]_0 = 0.05$ M; ●, 0.1 M; and ⊙, 0.2 M.

The rate of initiation is

$$r_i = 2k_{i3}[A] + 2k_{i3}[B] + 2k_{i3}[C] = 2k_{i3}C_t \quad (19)$$

The chain length is then (by substitution of eq. 11 for R_t)

$$\nu = 0.5k_pR_tC_t/2k_{i3}C_t = k_pC_t^{1/2}/4(k_{i3}k_t)^{1/2} \quad (20)$$

Substitution of eq. 20 into eq. 16 gives eq. 21, where k_a is the experimentally observed rate constant.

$$\ln([A] - [A]_e)/([A]_0 - [A]_e) = -k_{i3}(1 + 4\nu)t = -k_at \quad (21)$$

The kinetic expression (eq. 16 and 21) requires the exchange rate to be proportional to

$$k_{i3}[1 + k_pC_t^{1/2}/4(k_{i3}k_t)^{1/2}] \quad (22)$$

A plot of $k_{i3}(1 + 4\nu)$ as a function of $C_t^{1/2}$, the square root of the total polysulfide concentration, should give a straight line with y intercept equal to k_{i3}. Accordingly, the effect of a fourfold variation in total trisulfide concentration on the exchange rate was determined. The raw data in Table I are plotted according to eq. 21 in Figure 2. Again, the curvature is pronounced, requiring evaluation of the rates at constant degrees of conversion. The rates $k_{i3}(1 + 4\nu)$ obtained from the slopes of the curves in Figure 2 at values of $\ln([A]_0 - [A]_e)/([A] - [A]_e)$ of 0.2, 0.4, and 0.6 are given in Table V.

TABLE V

VARIATION OF $k_{i3}(1 + 4\nu)$ WITH TOTAL TRISULFIDE CONCENTRATION AT 140.0°

		$k_{i3}(1 + 4\nu) \times 10^5$, sec.$^{-1}$		
		—$\ln([A]_0 - [A]_e)/([A] - [A]_e)$—		
C_t	$C_t^{1/2}$	0.2	0.4	0.6
0.1001	0.316	4.5	4.9	5.1
0.2003	0.448	6.4	7.3	7.6
0.4006	0.633	9.3	9.7	10.3

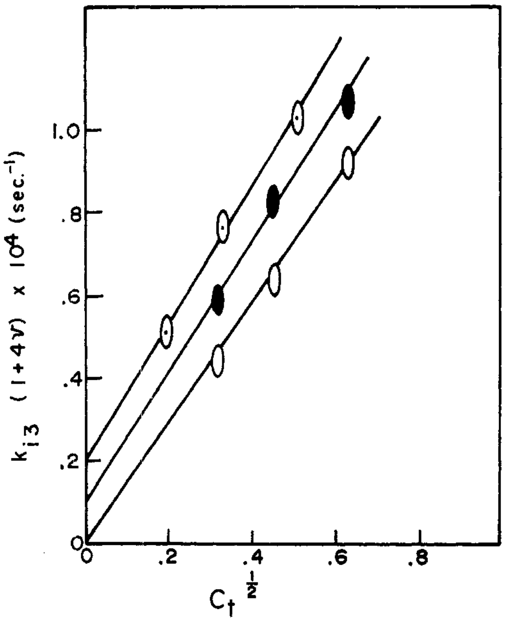


Figure 3.—Variation of $k_i(1 + 4\nu)$ with $C_t^{1/2}$ at various degrees of conversion: ○, ln ([A]$_0$ − [A]$_e$)/([A] − [A]$_e$) = 0.2; ●, 0.4; and ⊙, 0.6. The *y* intercept is displaced from zero for clarity.

The rates for each degree of conversion are plotted against $C_t^{1/2}$ in Figure 3. Straight lines intersecting the origin are obtained. The value of k_{i3} is small compared to the term containing $C_t^{1/2}$; thus it is experimentally indistinguishable from zero.

The experimental data are consistent with the proposed mechanism. In particular, this mechanism provides an explanation, previously lacking, for polysulfide disproportionation processes.

Experimental Section

Analyses.—All analyses were performed on an Aerograph Model A-350-B dual-column temperature-programming gas chromatograph. The 0.25 in. × 1 m. aluminum columns were packed with 15% SE-30 silicone gum on 60–80 mesh Gaschrom Z. In a typical analysis, the temperature was programmed from 100 to 160° at a rate of 10°/min. Injector temperature was maintained at 180°, detector temperature at 200°. Since very dilute solutions were used, the instrument was operated at near maximum sensitivity. With the specified chromatograph operating temperatures, no exchange was observed during analyses, as shown by analysis of a mixture of diethyl and di-*n*-propyl trisulfides. Chromatograms were recorded on a Minneapolis-Honeywell 0–1-mv. integrating recorder.

General Procedure for Kinetic Runs.—A benzene solution containing diethyl trisulfide, di-*n*-propyl trisulfide, and diphenyl ether as an internal standard was prepared and stored in the dark. A control experiment showed that essentially no exchange occurred after 1 month in the dark at room temperature. Two-milliliter aliquots of the trisulfide solution were pipetted into reaction tubes prepared by necking down 13 × 100 mm. test tubes. The tubes were cooled to −70° and sealed. No attempt was made to exclude air, since no change in rate was observed in a control experiment at 140° under nitrogen (see Tables II and III). Sample tubes were heated for varying periods of time in a thermostated bath controlled to within ±0.05°. Time intervals were monitored by means of a stopwatch. The reaction was stopped by quenching the reaction tubes in cold water. The tubes were then opened and the contents were analyzed. Triplicate analyses were performed on each sample tube; a precision of ±1% was obtained.

Preparation and Purification of Materials.—Reagent grade benzene was used without further purification. Nitrobenzene was freshly distilled before use. Reagent grade diphenyl ether was used without further purification.

Diethyl trisulfide was prepared by two methods.

A.—To a mixture of 31.1 g. (0.5 mole) of ethanethiol and 24.0 g. (0.75 g.-atom) of sulfur was added 3 drops of piperidine, according to the procedure described by Bloomfield.[9] The evolution of hydrogen sulfide was vigorous. (*Caution:* use hood.) The reaction mixture was allowed to stand at room temperature for 24 hr., then was fractionated *in vacuo*. The fraction boiling at 30–40° (0.1 mm.) contained 98.0% diethyl trisulfide, 1.7% diethyl disulfide, and 0.3% diethyl tetrasulfide by gas chromatographic analysis.

B.—The procedure described by Milligan, Saville and Swan[10] was utilized and proved to be the best method. A mixture of 54.5 g. (0.5 mole) of ethyl bromide, 124.1 g. (0.5 mole) of sodium thiosulfate pentahydrate, 200 ml. of water, and 200 ml. of ethanol was heated and stirred at reflux for 4 hr., at which time the solution was clear and homogeneous. Most of the ethanol was removed by distillation at reduced pressure, and the aqueous solution was cooled to room temperature. Phosphate buffer of pH 8 (100 ml.) and 37% aqueous formaldehyde (100 ml.) were added. Then a solution of 60.1 g. (0.25 mole) of sodium sulfide nonahydrate in 100 ml. of water was added in small portions with stirring over a period of 15 min., while the pH was maintained at 8 by dropwise addition of 10% aqueous hydrochloric acid. The reaction mixture was allowed to stand at room temperature for 4 hr., then was extracted three times with 150-ml. portions of benzene. The combined benzene extract was washed three times with water and dried over anhydrous sodium sulfate. The benzene was removed at reduced pressure and the residue was distilled. The diethyl trisulfide boiled at 40° (0.07 mm.). The product contained 99.3% diethyl trisulfide and 0.7% diethyl disulfide by gas chromatographic analysis. No diethyl tetrasulfide was detected.

Di-*n*-propyl trisulfide was prepared by the same procedures described for diethyl trisulfide. Method A yielded a product containing 92% di-*n*-propyl trisulfide, 6% di-*n*-propyl disulfide, and 2% di- and trisulfidic isomers, b.p. 50° (0.08 mm.). The product from method B contained 97.9% di-*n*-propyl trisulfide and 2.1% di-*n*-propyl disulfide. Tetrasulfide was not detected.

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