The Regioselective Reaction of Atomic Hydrogen with Unsymmetric Disulfides and Sulfides

Dennis D. Tanner,* Liying Zhang,[1] Markandu Vigneswaran, and Pramod Kandanarachchi

Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada

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Unsymmetric disulfides undergo solution phase reduction with atomic hydrogen regioselectively by displacement at the least hindered sulfur atom. The cleavage of the sulfur–sulfur bond forms mixtures of two thiol and two thiyl radicals. At the temperature at which the reactions are carried out, the thiyl radicals form symmetric disulfides by thiyl–thiyl radical coupling and not by thiyl radical displacement on the starting material. The reaction of atomic hydrogen with an unsymmetric sulfide is a cleavage that favors the formation of the most stable radical. The reaction of phenyl cyclohexyl sulfide produces benzene, cyclohexane, cyclohexyl thiol, and thiophenol. Benzene and cyclohexyl thiol produced from the cleavage of the phenyl–sulfur bond are proposed to arise from the α-scission of an intermediate formed by *ipso*-addition of atomic hydrogen to the benzene ring.

Introduction

In spite of the widespread interest in the chemistry of atomic hydrogen, studies involving organosulfur compounds are limited.[2] Earlier kinetic studies dealt with the vapor phase reactions of hydrogen atoms generated from the photolysis of simple alkyl thiols.[2] Interest in the biological effects of radiation in aqueous solution has prompted studies of the reactions of hydrogen atoms with cysteine and cystine.[3,4] The necessity of removing organic-bound sulfur from crude oils has directed attention to the reactions of hydrogen atoms with organosulfides, disulfides, and heterocyclic sulfur compounds. The vapor phase reactions of atomic hydrogen with dimethyl disulfide,[5] diethyl disulfide,[6] ethyl methyl disulfide,[6] bis(trifluoromethyl) disulfide,[7] and (dibutyl)disulfide[8] have more recently been reported. The vapor phase Hg-photosensitized decomposition of H_2 carried out in the presence of an unsymmetric disulfide, ethyl methyl disulfide,[7] was shown to involve a chain decomposition where the primary processes, eqs 1 and 2

$$H^\bullet + CH_3SSCH_2CH_3 \rightarrow CH_3SH + C_2H_5S^\bullet \quad (1)$$

$$H^\bullet + CH_3SSCH_2CH_3 \rightarrow C_2H_5SH + CH_3S^\bullet \quad (2)$$

also included thiyl exchange reactions, eqs 3 and 4.

$$CH_3S^\bullet + CH_3SSC_2H_5 \rightarrow CH_3SSCH_3 + C_2H_5S^\bullet \quad (3)$$

$$C_2H_5S^\bullet + CH_3SSC_2H_5 \rightarrow C_2H_5SSC_2H_5 + CH_3S^\bullet \quad (4)$$

Reactions with Disulfides. The Hg-sensitized decomposition of H_2 in the presence of $C_2H_5SSC_2H_5$ yielded C_2H_5SH as the only retrievable product.[6] The principal elementary reaction between the H atom and the diethyl disulfide molecule was assumed to be a radical displacement reaction (eq 5). Kinetic determinations in the vapor phase at various temperatures, in the presence of added ethylene, yielded an Arrhenius equation for reaction 5 relative to the known rate constant for the addition of atomic hydrogen to ethylene.[6,9] The reaction of dibutyl disulfide with hydrogen atoms generated in a flow system by a microwave discharge at room temperature was studied by Amano and co-workers.[8] 1-Butanethiol, butane, and 1-butene were the main products. Radical displacement on sulfur was proposed to be the primary process. A metastable intermediate formed from the addition of H• to one of the sulfur atoms was assumed to decompose to a thiol and thiyl radical.

$$H^\bullet + C_2H_5SSC_2H_5 \rightarrow C_2H_5SH + C_2H_5S^\bullet \quad (5)$$

$$k = (4.7 \pm 0.6) \times 10^{10} \exp[(-1710 \pm 69)/RT]\ M^{-1}\ s^{-1}$$

The reaction of ethyl methyl disulfide with atomic hydrogen was studied by Strausz and co-workers using the Hg-sensitized photodecomposition of H_2 to generate the atoms.[6] Two parallel and competing processes (eqs 1 and 2 and 3 and 4) were proposed to account for the formation of the product mixture. The very high quantum yields obtained for the formation of CH_3SSCH_3 and $C_2H_5SSC_2H_5$ suggest that the thiyl radicals propagate a chain of radical exchange reactions to form the two symmetric disulfides, eqs 3 and 4. Termination of the chain and the final fate of the thiyl radicals were postulated as both combination and disproportionation processes, although the products of disproportionation were not detected.[6]

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[9] The value previously reported for the reaction of atomic hydrogen with an olefin[10] has been redetermined[11] for the solution phase reaction of 1-octene. Since the vapor phase rate constants for the addition of hydrogen to ethylene and propylene are experimentally indistinguishable,[12] the value for the rate constant for the reaction of an acetone solution of 1-octene, $9.5 \times 10^8\ M^{-1}\ sec^{-1}$ (25 °C), can be used as a minium estimate for the solution phase value for the reaction of atomic hydrogen with ethylene.

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Scheme 1

$$H^{\bullet} + C_2H_5SC_2H_5 \longrightarrow C_2H_5S^{\bullet}HC_2H_5 \quad (6)$$

$$C_2H_5S^{\bullet}HC_5H_5 \longrightarrow C_2H_5^{\bullet} + C_2H_5SH \quad (7)$$

$$2C_2H_5^{\bullet} \longrightarrow C_2H_4 + C_2H_6 \quad (8)$$

$$2C_2H_5^{\bullet} \longrightarrow C_4H_{10} \quad (9)$$

$$C_2H_4 + H^{\bullet} \longrightarrow C_2H_5^{\bullet} \quad (10)$$

Thiyl radicals react considerably more slowly with disulfides[6] than H atoms since the vapor phase rate constant for reaction 1 is 2.6×10^9 M^{-1} s^{-1} at 25 °C and the rate constants for reactions 3 and 4 are 0.014×10^9 and 0.0078×10^9 M^{-1} s^{-1}, respectively, at 25 °C.[6,9]

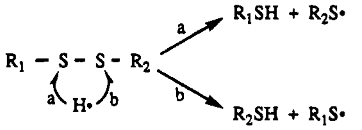
Reaction with Sulfides. Ekwenchi *et al.*[13] studied the vapor phase reaction of diethyl sulfide with atomic hydrogen, over the temperature range of 298–461 K. The major products were ethyl thiol, ethylene, ethane, and *n*-butane. The product yields obtained for these Hg-sensitized reactions were rationalized by the mechanistic sequence shown in Scheme 1. The mechanism assumes that the hydrogen atom attacks exclusively at sulfur, forming a metastable adduct which subsequently decomposes to give alkyl thiol and an alkyl radical, eqs 6 and 7. The rate of the reaction of atomic hydrogen with diethyl sulfide ($k = (4.7 \pm 0.9) \times 10^{10} \exp[(-3797 \pm 152)/RT]$ M^{-1} s^{-1}) was determined from a plot of the relative rate of the displacement reaction *vs* the previously determined rate of addition to ethylene (eq 10).[9,13]

Results and Discussion

The Reaction of Atomic Hydrogen with Disulfides. The reaction of an acetone solution of dibutyl disulfide with atomic hydrogen generated in a microwave discharge of H_2 yields 1-butanethiol as the only retrievable product. This result agrees with the reaction mechanism proposed by Strausz[6] which postulates that the principal elementary reaction between a H atom and the dibutyl disulfide molecule is a radical displacement reaction, eq 11. The regioselective cleavage of an unsymmetric disulfide bond was investigated by allowing several unsymmetrically substituted disulfides to undergo reactions with atomic hydrogen. In order to test substituent steric effects, 1-butyl *tert*-butyl disulfide, *sec*-butyl *tert*-butyl disulfide, and *sec*-butyl 1-hexyl disulfide were selected as model disulfides; see Table 1. Thiols and disulfides were products of the reactions. The observation that the ratios of the product thiols, 1-butanethiol/*tert*-butanethiol, 2-butanethiol/*tert*-butanethiol, and 1-hexanethiol/2-butanethiol, were 2.16, 1.34, and 1.36, respectively, suggests that displacement on sulfur with the primary substituent is favored over that with a secondary or tertiary substituent. This displacement pattern is no doubt a reflection of the steric demands imposed by the substituents on the rate-determining step leading to the products.

$$H^{\bullet} + C_4H_9SSC_4H_9 \rightarrow C_4H_9SH + C_4H_9S^{\bullet} \quad (11)$$

The mechanism for the reaction of a disulfide with atomic hydrogen can be rationalized by displacement on sulfur either by direct displacement or by α-scission of the metastable intermediate radical formed by addition of a hydrogen atom to one of the sulfur atoms (eq 12). Two thiols and two thiyl radicals are formed by paths a and b. The fate of the thiyl radicals is either to react with hydrogen (eqs 20 and 21), to dimerize (eqs 15–17), to exchange with thiol (eq 22), or to undergo radical exchange reactions with starting material to form the two symmetric disulfides, eqs 18 and 19.



(12)

$$R_1SSR_2 + H^{\bullet} \xrightarrow{k_1} R_1SH + R_2S^{\bullet} \quad (13)$$

$$R_1SSR_2 + H^{\bullet} \xrightarrow{k_2} R_2SH + R_1S^{\bullet} \quad (14)$$

$$R_1S^{\bullet} + R_2S^{\bullet} \xrightarrow{k_3} R_1SSR_2 \quad (15)$$

$$R_1S^{\bullet} + R_1S^{\bullet} \xrightarrow{k_4} R_1SSR_1 \quad (16)$$

$$R_2S^{\bullet} + R_2S^{\bullet} \xrightarrow{k_5} R_2SSR_2 \quad (17)$$

$$R_1S^{\bullet} + R_1SSR_2 \xrightarrow{k_6} R_1SSR_1 + R_2S^{\bullet} \quad (18)$$

$$R_2S^{\bullet} + R_1SSR_2 \xrightarrow{k_7} R_2SSR_2 + R_1S^{\bullet} \quad (19)$$

$$R_1S^{\bullet} + H^{\bullet} \xrightarrow{k_8} R_1SH \quad (20)$$

$$R_2S^{\bullet} + H^{\bullet} \xrightarrow{k_9} R_2SH \quad (21)$$

$$R_2S^{\bullet} + R_1SH \overset{k_{10}}{\rightleftharpoons} R_2SH + R_1S^{\bullet} \quad (22)$$

The thiyl/thiol exchange reaction (eq 22), although a fast reaction (2×10^9 M^{-1} s^{-1}),[14] is not significant at very low conversion (*i.e.*, low [RSH]) since the ratio of $[R_1SH]/[R_2SH]$ is relatively constant at <13% conversion; see Tables 2–4. The two symmetric disulfides are formed by thiyl–thiyl coupling or thiyl displacement on starting material; see eqs 18 and 19. The kinetic expressions for the formation of the symmetric disulfides by these two pathways show a dependence on the concentration of the starting material; see eqs 23 and 24. If the radical displacement reaction contributes significantly to the formation of the symmetric disulfides, the amount of symmetric disulfides formed would be dependent upon the concentration of R_1SSR_2. The three starting disul-

$$d[R_1SSR_1]/dt = k_4[R_1S^{\bullet}]^2 + k_6[R_1S^{\bullet}][R_1S^{\bullet}][R_1SSR_2] \quad (23)$$

$$d[R_2SSR_2]/dt = k_5[R_2S^{\bullet}]^2 + k_7[R_2S^{\bullet}][R_1SSR_2] \quad (24)$$

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Table 1. The Product Distributions from the Reactions of Several Disulfides with Atomic Hydrogen[a]

			% of product				
reaction	starting material R_1SSR_2	conversion (%)	R_1SH	R_2SH	R_1SSR_1	R_2SSR_2	R_1SH/R_2SH[b]
1	R_1 = *n*-C_4H_9 R_2 = *tert*-C_4H_9	5.72	51.6	24.1	5.38	18.9	2.16
2	R_1 = *sec*-C_4H_9 R_2 = *tert*-C_4H_9	4.30	43.8	33.2	6.88	16.1	1.34
3	R_1 = *n*-C_6H_{13} R_2 = *sec*-C_4H_9	3.43	42.7	33.4	9.86	14.0	1.36

[a] Substrate concentration, 0.05 M in acetone; reaction temperature, −78 °C; pressure, 3.00 Torr; H_2 flow rate, 0.5 mL/min. [b] Ratio obtained from the extrapolation when $[R_1SSR_2] \rightarrow 0$ in Figures 1−3.

Table 2. The Product Distribution from the Reaction of 1-Butyl *tert*-Butyl Disulfide with Atomic Hydrogen[a]

		% of product					
concentration (M)	conversion (%)	1-BuSH	*t*-BuSH	*t*-BuSSBu-*t*	1-BuSSBu-1	total of symmetric disulfides	1-BuSH/*t*-BuSH
0.0466	13.8	51.6	24.1	18.9	5.38	24.3 ± 1.1	2.14
0.1079	12.5	50.9	23.4	17.5	8.18	25.7 ± 0.3	2.17
0.2427	6.9	51.7	22.1	17.2	8.95	26.1 ± 0.7	2.33
0.4219	5.7	50.7	23.8	17.3	8.14	25.4 ± 0.05	2.09
						25.4 ± 0.5[b]	2.18 ± 0.07[b]

[a] Solution in acetone; reaction temperature, −78 °C; pressure, 3.00 Torr; H_2 flow rate, 0.5 mL/min. [b] Average of first four entries.

Table 3. The Product Distribution from the Reaction of *sec*-Butyl *tert*-Butyl Disulfide with Atomic Hydrogen[a]

		% of product					
concentration (M)	*t*-BuSSBu-2 left (%)	2-BuSH	*t*-BuSH	*t*-BuSSBu-*t*	2-BuSSBu-2	total of symmetric disulfides	2-BuSH/*t*-BuSH
0.019	92.3	45.4	33.9	6.50	14.2	20.7 ± 1.0	1.34
0.050	95.7	43.8	33.2	6.88	16.1	23.0 ± 1.3	1.32
0.080	97.0	44.6	33.5	5.92	16.0	21.9 ± 0.2	1.33
0.178	97.9	45.5	34.7	5.78	14.0	19.8 ± 2.0	1.31
0.647	99.0	43.7	33.1	6.90	16.4	23.2 ± 1.5	1.32
						21.7 ± 1.2[b]	1.32 ± 0.01[b]

[a] Solution in acetone; reaction temperature, −78 °C; pressure, 3.00 Torr; H_2 flow rate, 0.5 mL/min. [b] Average of first four entries.

Table 4. The Product Distribution from the Reaction of *sec*-Butyl 1-Hexyl Disulfide with Atomic Hydrogen[a]

		% of product					
concentration (M)	conversion (%)	1-HexSH	2-BuSH	2-BuSSBu-2	1-HexSSHex-1	total of symmetric disulfides	1-HexSH/2-BuSH
0.023	4.5	42.1	32.9	14.2	10.8	25.0 ± 0.6	1.28
0.056	3.4	42.7	33.4	14.0	9.9	23.9 ± 0.4	1.29
0.110	3.2	43.6	33.8	13.0	9.7	22.6 ± 1.7	1.29
0.297	3.0	42.6	32.7	14.2	10.5	24.7 ± 0.4	1.30
0.478	2.1	42.0	32.5	14.2	11.2	25.48 ± 1.1	1.29
						24.3 ± 0.8[b]	1.29 ± 0.03[b]

[a] Solution in acetone; reaction temperature, −78 °C; pressure, 3.00 Torr; H_2 flow rate, 0.5 mL/min. [b] Average of first four entries.

fides were subjected, at different concentration, to reaction with atomic hydrogen. The relative yields of the symmetric disulfides did not change when decreasing concentrations of starting material were used; see Tables 2−4. Under the reaction conditions, the symmetric disulfides appear to be formed primarily by thiyl−thiyl coupling, eqs 16 and 17. The absence of the thiyl radical exchange reactions in the solution phase reaction is not surprising since the difference in temperature (~100 °C) can easily account for this mechanistic difference.

The concentrations of the two thiols are dependent upon the concentration of hydrogen atoms, eqs 25 and 26. At very low concentrations of hydrogen atoms (*e.g.*,

$$d[R_1SH]/dt = k_1[H^\bullet][R_1SSR_2] + k_8[H^\bullet][R_1S^\bullet] \qquad (25)$$

$$d[R_2SH]/dt = k_2[H^\bullet][R_1SSR_2] + k_9[H^\bullet][R_2S^\bullet] \qquad (26)$$

as $[H^\bullet]$ approaches 0), the probability of a radical−radical combination becomes very small and the ratio of product thiols approaches the ratio of rate constants for addition, eq 27; see Figures 1−3.

$$[R_1SH]/[R_2SH] = k_1/k_2 \qquad (27)$$

The ratio of the two thiols at $[H^\bullet] = 0$ (*i.e.*, 0 H_2 flow rate) and $[R_1SSR_2] = 0$ (Figures 1−3) defines the regioselectivity of attack at sulfur and is calculated from the plots of the ratio of thiols at a concentration of hydrogen = 0. The calculated results are listed in Table 5. The ratio of thiols listed appears to result from the energy differences imposed on the transition state by the bulk of the alkyl substituents. Since the ratio of thiols is dependent upon the hydrogen flow rate, Figures 1−3, the dependence can be interpreted as being due to the reaction of a thiyl radical with atomic or molecular hydrogen. Although bimolecular radical−radical reactions even at diffusion-controlled rates are not usually favored (eqs 20 and 21), the reaction of a thiyl radical with molecular hydrogen (eq 28) is extremely unattractive since its activation energy must be endoergonic by a minimum amount of 16 kcal/mol (*D*(RS−H) = 88 kcal/mol, *D*(H−H) = 104 kcal/mol).

$$RS^\bullet + H_2 \rightarrow RSH + H^\bullet \qquad (28)$$

The Reaction of Atomic Hydrogen with Sulfides. In order to investigate the selectivity of the cleavage of

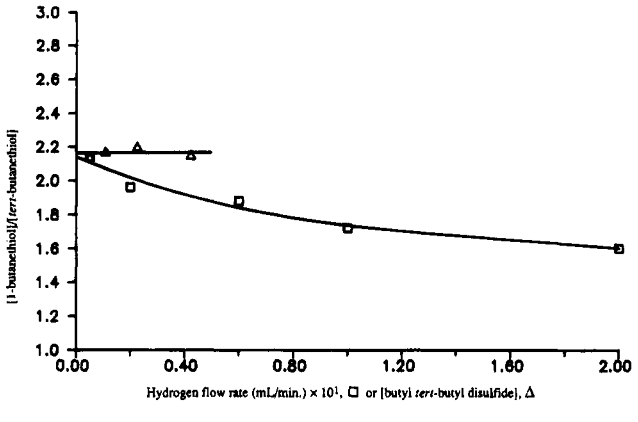


Figure 1. Plot of the hydrogen flow rate and the concentration of butyl *tert*-butyl disulfide *vs* the ratio of [1-butanethiol]/[*tert*-butanethiol].

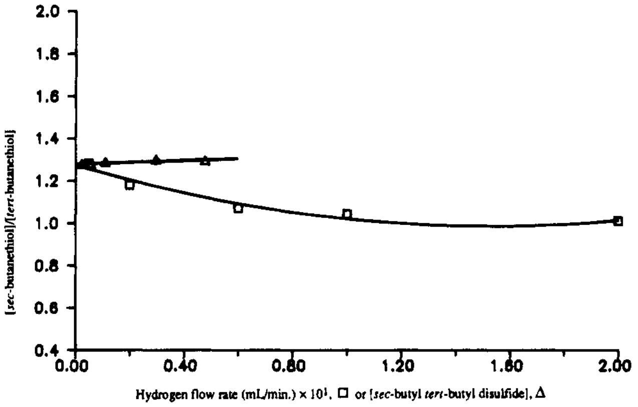


Figure 2. Plot of the hydrogen flow rate and the concentration of *sec*-butyl *tert*-butyl disulfide *vs* the ratio of [*sec*-butanethiol]/[*tert*-butanethiol].

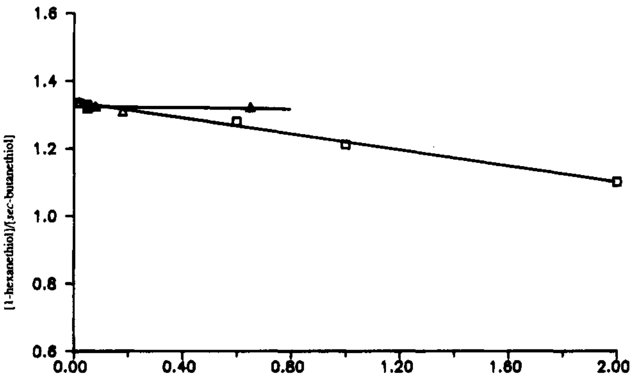
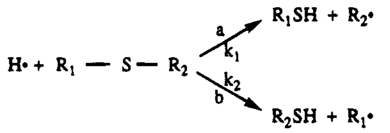


Figure 3. Plot of the hydrogen flow rate and the concentration of sec-butyl hexyl disulfide *vs* the ratio of [hexanethiol]/[*sec*-butanethiol].

the sulfide bond, four unsymmetric compounds, *tert*-butyl hexyl sulfide, *tert*-butyl 2-octyl sulfide, *sec*-butyl hexyl sulfide, and hexyl cyclohexyl sulfide, were selected as substrates for reaction with atomic hydrogen. The results of these hydrogenolysis reactions are listed in Table 6. Displacement on sulfur is observed since the products are derived from the fragmentation of the alkyl−sulfur bond. When atomic hydrogen was passed over an acetone solution of either of the dialkyl sulfides (0.5 M), the products of the reactions were mixtures of two alkanes, two thiols, and three disulfides; see Table 6. The following mechanisms can be proposed for the reaction of atomic hydrogen with a sulfide. The hydrogen atom adds to the sulfide and forms a metastable intermediate $R_2S{\cdot}HR_1$, followed by cleavage or a direct S_H2 displacement; either process yields a thiol and an alkyl radical (eq 29). The two thiols and two alkyl radicals



(29)

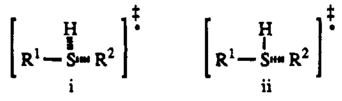
are formed by paths a and b. The alkane derived from the alkyl radical, if not formed by disproportionation, is formed by a radical−radical combination reaction,[15] eq 30. A second competitive reaction is available to the alkyl radicals formed in the presence of a thiol, eq 31. The

$$R^{\bullet} + H^{\bullet} \xrightarrow{k_{R^{\bullet}}} RH \qquad (30)$$

$$R^{\bullet} + R'SH \xrightarrow{k_t} RH + R'S^{\bullet} \qquad (31)$$

rate constant for the reaction of primary alkyl radical with *tert*-BuSH has been reported as $\sim 10^6$ L mol^{-1} sec^{-1}.[16] Although disproportionation and combination reactions of alkyl radicals are diffusion-controlled, olefin formed by disproportionation will be rapidly reduced, and under the reaction conditions (−78 °C, 0.5 M in acetone), the combination products from the alkyl radicals will only be formed in minor amounts.[15] Alkane formation by transfer with a hydrogen atom or a thiol, eqs 30 and 31, appears to be the most reasonable reaction. The thiyl radicals formed by this transfer step either dimerize to give disulfide or react with a hydrogen atom to regenerate a thiol. The products from the reactions of the four unsymmetric dialkyl sulfides are listed in Table 6. The selectivity of the displacement reaction can be calculated from the yields of the sulfur-containing compounds, *i.e.*, thiols and disulfides, and from the yields of the hydrocarbons formed, $(R_1H + R_2S)/(R_2H + R_1S) = k_1/k_2$; see Table 7. The qualitative observation that the relative rates of fragmentation favor the displacement of the most stable radical (Table 7) is put on a quantitative scale by applying the Evans−Polanyi relationship to the relative rates of fragmentation.[17] The stability of the radical ejected is directly proportional to its relative rate of fragmentation, k_{x°/k_{1°, where x° = primary, secondary, or tertiary alkyl radicals and the slope is 0.25 (see Figure 4). An Evans−Polanyi plot with a slope of 0.25 can be interpreted as representing a reaction with a transition state in which the carbon−sulfur bond is 25% broken.

The value of the slope is consistent with the transition state from either direct displacement i or the fragmentation of the trivalent sulfur intermediate (ii). By the same



i ii

mechanism, the products of the reduction of an aryl alkyl sulfide would not be expected to undergo aryl radical cleavage; however, when an acetone solution (0.1 M) of cyclohexyl phenyl sulfide was hydrogenalized, a substantial amount (12−15%) of benzene was produced. The

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Table 5. The Regioselectivities of the Reactions of Atomic Hydrogen with the Unsymmetric Disulfides[a]

reaction	$[R_1SH]/[R_2SH]$[b]	a:b (%)[c]	R_1/R_2[d]
1-butyl *tert*-butyl disulfide (Table 2)	2.16	68:32	primary/tertiary
sec-butyl *tert*-butyl disulfide (Table 3)	1.34	57:43	secondary/tertiary
sec-butyl 1-hexyl disulfide (Table 4)	1.36	56:44	primary/secondary

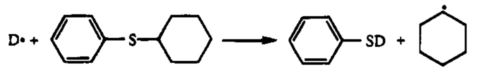
[a] Acetone solutions of substrates, −78 °C. [b] The ratio of thiols obtained from the plots, Figures 1−3 at zero $[R_1SSR_2]$ or $[H^\bullet]$. [c] Percentage of attack by path a or b, eq 12. [d] Primary/tertiary = 2.16 or secondary/tertiary·primary/secondary = 1.82; primary/tertiary = 1.99 ± 0.16.

Table 6. The Distribution of Products from the Reactions of Several Sulfides with Atomic Hydrogen at −78 °C[a]

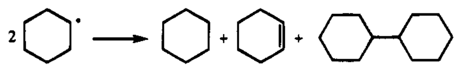
				mol % of products						
reaction	starting material R_1SR_2	time (min)	conversion (%)	R_1H	R_2H	R_2SH	R_1SH	R_1SSR_2	R_1SSR_1	R_2SSR_2
1	R_1 = *tert*-C_4H_9 R_2 = 1-C_6H_{13}	4	11.5	49.6	1.7	40.7	2.5	0.7	0	4.9
2	R_1 = *tert*-C_4H_9 R_2 = *sec*-C_8H_{17}	7	27.0	47.9	6.1	36.4	4.1	0.3	0	4.9
3	R_1 = *sec*-C_4H_9 R_2 = 1-C_6H_{13}	6	21.4	43.1	3.0	33.1	9.5	3.6	0	7.7
4[b]	R_1 = C_6H_5 R_2 = *c*-C_6H_{11}	3	8.9	9.0	46.9[c]	4.0	37.5	0	2.2	0
5[b]	R_1 = *c*-C6H11 R_2 = 1-C_6H_{13}	30	23	37.7	11.6	–	–	–	–	–

[a] 0.5 M in acetone; hydrogen flow rate, 4 mL/min. [b] 0.1 M in acetone. [c] Trace of cyclohexene found in the product.

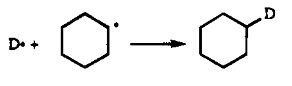
reaction of this sulfide with deuterium atoms produced a similar mixture of products. An analysis of the pattern of deuteration in each product gave insight into the detailed mechanism of the reduction; see Table 8. The fragmentation of the intermediate trivalent sulfur radical, as expected, yielded as the major fragment a cyclohexyl radical, eq 32. Although combination and disproportionation yield small amounts of undeuterated cyclohexane, cyclohexene, and bicyclohexyl, eq 33, the major product was not monodeuterated cyclohexane, eq 34, but undeuterated cyclohexane. Since no products were detected as resulting from abstraction from the solvent, the only source of protium was the substrate cyclohexyl phenyl sulfide. The mass spectrum of the starting material showed that the starting sulfide contained 76% of the deuterium that was incorporated into the product mixture. Incorporation of deuterium into the starting material necessitates a deuterium-protium exchange reaction, eqs 35 and 36. Incorporation of protium into the cyclohexane no doubt involves a disproportionation reaction between a cyclohexadienyl radical and a cyclohexyl radical, eq 36. However, if deuterium or protium adds to the *ipso*-position of the aryl sulfide, α-scission of the phenyl−sulfur bond yields either benzene or deuteriobenzene, eq 37.



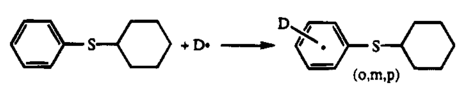
(32)



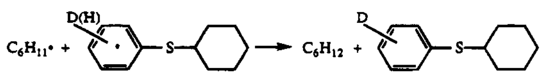
(33)



(34)



(35)



(36)

Table 7. The Selectivities of the Displacement of Atomic Hydrogen on Sulfur

reaction[a]	R_1	R_2	$[R_1H + R_2S]$	$[R_2H + R_1S]$	k_1/k_2[c]
1	$(CH_3)_3C$	1-C_6H_{13}	100.8	4.9	20.6
2	$(CH_3)_3C$	*sec*-C_4H_9	99.3	10.1	6.2[b]
3	*sec*-C_6H_9	1-C_6H_{13}	95.2	16.1	5.9
5	C_6H_{11}	1-C_6H_{13}	37.7	11.6	3.3[b]

[a] Taken from the data in Table 6. [b] Calculated from the ratio of hydrocarbons. [c] The indirect calculation of the tertiary/primary selectivity, (tertiary/secondary)/(secondary/primary) = (5.9)(6.2) = 36.6.

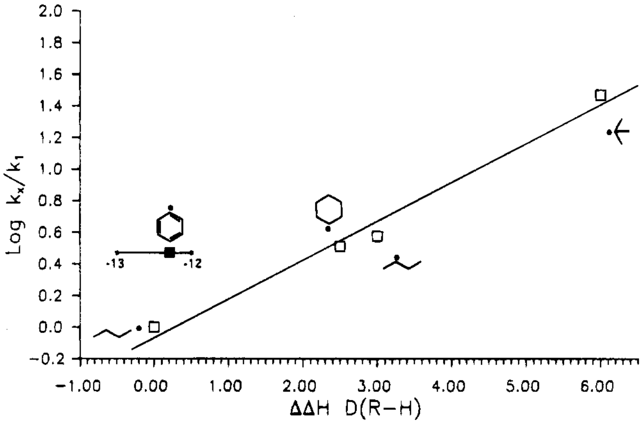
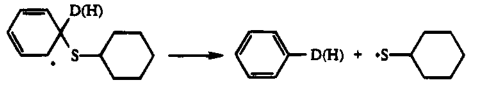


Figure 4. Evans−Polanyi plot of the ratio of the rates of fragmentation of R•, $k_x \cdot /k_1 \cdot$, *vs* the difference in *D*(R−H).



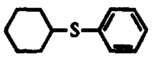
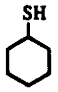
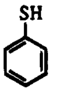
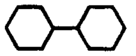
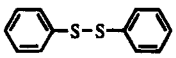
(37)

Experimental Section

Materials. Dibutyl disulfide (98+%), dihexyl sulfide (95+%), butanethiol (99+%), *sec*-butyl thiol (98+%), *tert*-butyl thiol (99+%), cyclohexanethiol (97+%), and thiophenol (99+%) were obtained from Aldrich, checked for purity by GC, and used as received.

***n*-Butyl *tert*-butyl disulfide** was prepared according to the literature procedure from the reaction of 1-bromobutane (137 g, 1.00 mol), excess sodium thiosulfate, and sodium *tert*-butylthiolate (90 g, 1.00 mol).[18] The pure disulfide (50 g, 0.28 mol) was isolated by distillation: bp 196−198 °C; ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, *J* = 7 Hz), 1.26 (s, 9H), 1.32 (m,

Table 8. The Reaction of Atomic Deuterium[a] with Cyclohexyl Phenyl Sulfide[b,c]

Reactant (0.1 M)	Products (%)						
							
0.086 M	12.7	60.1	6.1	4.1	14.4	1.1	1.6
[d] (d_0, d_1, d_2)	(d_0, d_1, d_2)	(d_0, d_1)	(d_0)	(d_0)	(d_0, d_1, d_2)	(d_0)	(d_0, d_1, d_2)
(0.71, 0.26, 0.01)	(0.23, 0.76, 0.02)	(0.84, 0.16)	(1.00)	(1.00)	(0.82, 0.14, 0.04)	(1.00)	(0.68, 0.24, 0.08)

$$\frac{\text{D (Starting Material)}}{\text{D (Total + S-D)}} = 75.7\%$$

[a] Deuterium flow rate, 4 mL/min, 30 min. [b] Solvent, acetone, −78 °C. [c] RSD and ArSD exchange with H_2O during mass spectral analysis produced protiated sulfur. [d] The distribution of deuterium in the M$^+$ fragment of each compound.

2H), 1.55 (m, 2H), 2.67 (t, 2H, $J = 7$ Hz); EI$^+$ (GC/MS, VG-70) *m/z* 178 (M$^+$), 122, 87, 79, 57; IR (vapor phase) ν 2969, 1464, 1367, 1275, 1168, 746 cm^{-1}. Anal. Calcd for $C_8H_{18}S_2$: C, 53.87; H, 10.17; S, 35.95. Found: C, 53.98; H, 10.39; S, 35.60.

***sec*-Butyl *tert*-butyl disulfide** was prepared from 2-bromobutane (41.6 g, 0.3 mol) and *tert*-butanethiol (4.5 g, 0.05 mmol) according to the procedure used for the synthesis of *n*-butyl *tert*-butyl disulfide.[18] The product was isolated in a 70% yield by fractional distillation: bp 197−198 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.98 (t, 3H, $J = 7$ Hz), 1.26 (d, 3H, $J = 7$ Hz), 1.31 (s, 9H), 1.52 (m, 1H), 1.68 (m, 1H), 2.74 (m, 1H); IR (vapor phase) ν 2971, 1461, 1369, 1287, 1165, 1006, 790 cm^{-1}. Anal. Calcd for $C_8H_{18}S_2$: C, 53.88; H, 10.17; S, 35.96. Found: C, 53.48; H, 10.22; S, 35.75.

***sec*-Butyl *n*-hexyl disulfide** was prepared using the standard procedure described for the preparation of *n*-butyl *tert*-butyl disulfide.[18] 1-Bromohexane (8.2 g, 0.05 mol) and *sec*-butanethiol (4.5 g, 0.05 mol) were used in the reaction. The product was isolated in a 69% yield (7.2 g, 0.035 mol): bp 222−223 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.89 (t, 3H, $J = 7$ Hz), 0.98 (t, 3H, $J = 7.5$ Hz), 1.20−1.80 (m, 13H), 2.60−2.85 (m, 3H). Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74. Found: C, 58.37; H, 10.69.

***tert*-Butyl hexyl sulfide** was prepared by alkylating the sodium salt of *tert*-butanethiol (9 g, 0.1 mol) with 1-bromohexane (16.6 g, 0.1 mol) in boiling ethanol (25 mL, 1 h).[19] The product was isolated by pouring the reaction mixture onto ice, and the crude oily layer was extracted with diethyl ether and dried over anhydrous $MgSO_4$. Distillation of this material gave 7.3 g (0.035 mol) of the pure sulfide in a 35% yield: bp 198−199 °C; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 33H, $J = 7$ Hz), 1.26 (m, 15H), 1.55 (m, 2H), 2.50 (t, 2H, $J = 7.5$ Hz). Anal. Calcd for $C_{10}H_{22}S$: C, 68.89; H, 12.71. Found: C, 68.92; H, 12.63.

***tert*-Butyl 2-octyl sulfide** was prepared using the same procedure used for the synthesis of *tert*-butyl *n*-hexyl sulfide. 2-Bromooctane (9.6 g, 0.05 mol) and *tert*-butanethiol (4.5 g, 0.05 mol) were used in the synthesis. The product was isolated in a 62% yield (6.3 g, 0.03 mol): bp 65−67 °C/0.5 mmHg; ^{1}H NMR (200 MHz, $DDCl_3$) δ 0.85 (t, 3H, $J = 7$ Hz), 1.20−1.55 (m, 22H, max 1.32, 9H), 2.65 (m, 1H). Anal. Calcd for $C_{12}H_{26}S$: C, 71.21; H, 12.95. Found: C, 71.61; H, 12.52.

***sec*-Butyl hexyl sulfide** was prepared using the standard procedure.[19] 1-Bromohexane (8.25 g, 0.05 mol) and *sec*-butanethiol (4.5 g, 0.05 mol) were used in the reaction. The product was isolated in a 81% yield (7.2 g, 0.04 mol): bp 69−70 °C/1.0 mmHg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, $J = 7$ Hz), 0.98 (t, 3H, $J = 7.5$ Hz), 1.26 (d, 3H, $J = 6.5$ Hz), 1.26−1.45 (m, 8H), 1.45−1.65 (m, 2H), 2.50 (t, 2H, $J = 7.5$ Hz), 2.65 (m, 1H). Anal. Calcd for $C_{10}H_{22}S$: C, 68.89; H, 12.71. Found: C, 68.68; H, 12.66.

Hexyl cyclohexyl sulfide was prepared according to the standard procedure.[19] 1-Bromohexane (8.25 g, 0.05 mol) and cyclohexanethiol (5.8 g, 0.05 mmol) yielded 8.2 g (0.04 mol) of pure sulfide: bp 123−124 °C/2.5 mmHg; ^{1}H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, $J = 7$ Hz), 1.26−1.55 (m, 14H), 1.72 (m, 2H), 1.92 (m, 2H), 2.50 (t, 2H, $J = 7.5$ Hz), 2.60 (m, 1H); EI$^+$ *m/z* 209.8 (M$^+$). Anal. Calcd for $C_{12}H_{24}S$: C, 71.92; H, 12.07. Found: C, 71.68; H, 12.46.

Cyclohexyl phenyl sulfide was prepared using the standard procedure.[19] The pure compound was prepared from cyclohexyl bromide and the sodium salt of thiophenol: bp 242−243 °C; ^{1}H NMR (300 MHz, $DCCl_3$) δ 1.30−1.50 (m, 5H), 1.62−1.70 (m, 1H), 1.79−1.88 (m, 2H), 2.01−2.11 (m, 2H), 3.12−3.22 (m, 1H), 7.20−7.35 (m, 3H), 7.42−7.50 (m, 2H); ^{13}C NMR (300 MHz, $DCCl_3$) δ 25.72, 25.95, 33.27, 126.44, 128.63, 161.76, 135.17. Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67. Found: C, 75.24; H, 8.64; S, 16.43.

General Procedure for the Reaction of Disulfides or Sulfides with Atomic Hydrogen and the Quantitative GC Analysis of the Products. An aliquot of a solution of the disulfide or sulfide in acetone was placed in the U-shaped reactor. The reactor was cooled to −78 °C. The reaction system pressure was controlled at 3.00 Torr with a ratio of 500:1 to 12:1 He:H_2. The reaction was carried out for 1 min for the disulfide reactions and from 6−15 min for the sulfide reaction. After the reaction, the product mixture was transferred to a vial, cooled in dry ice, and analyzed by GC.

The product mixtures were analyzed using a 105 m × 0.25 mm × 0.5 μm Rt$_x$-1 capillary column. GC analysis was carried out using a Varian 6000 chromatograph equipped with a hydrogen flame detector interfaced to a Varian Vista CDS 401 chromatography data system. The area ratios were converted to mole ratios for quantitative determination by using correction factors which were obtained by preparing a standard solution of known concentration of the authentic compounds and an internal standard.

The competitive reactions were carried out using equimolar amounts of the two disulfides as the reaction reached approximately 20% completion. The reactivities were found to be 1:1, calculated from the disappearance of the starting material.

Identification of Products. Hexane, octane, *tert*-butane, cyclohexane, benzene, butanethiol, *tert*-butanethiol, *sec*-butanethiol, hexanethiol, cyclohexanethiol, thiophenol, *sec*-octanethiol, di-*tert*-butyl disulfide, di-*sec*-butyl disulfide, diphenyl

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[18] Alonso, M. E.; Aragona, H. In *Organic Syntheses*; Sheppard, W. A., Ed.; John Wiley & Sons: New York, 1980; Vol. 58, pp 147−152.

[19] Wagner, R. B.; Zook, H. D. *Synthetic Organic Chemistry*; John Wiley & Sons: New York, 1953; p 787.

disulfide, and di-*n*-butyl sulfide were identified by comparison of their GC retention times and their GC/MS and GC/IR spectra with those of the authentic compounds.

Dicyclohexyl disulfide was synthesized according to the literature procedure.[18] Cyclohexyl bromide (16.3 g, 0.1 mol), excess $Na_2S_2O_3$, and cyclohexanethiol (11.62 g, 0.1 mol) yielded 85% (20 g, 0.085 mol): bp 195 °C/20 mmHg; ^1H NMR (200 MHz, $DCCl_3$) δ 1.20–1.40 (m, 3H), 1.40–1.60 (m, 1H), 1.6–1.8 (m, 4H), 2.1–2.1 (m, 2H), 4.1–4.2 (m, 1H); EI^+ (GC/MS, VG-70) *m/z* 230 (M^+), 148, 113, 83, 73, 67, 55, 41; IR (vapor phase) ν 2940, 2871, 1453, 1341, 1263, 1198, 993 cm^{-1}. Anal. Calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62. Found: C, 62.60; H, 9.46.

Dihexyl disulfide was synthesized according to the standard procedure.[18] 1-Bromohexane (16.5 g, 0.1 mol), excess $Na_2S_2O_3$, and *n*-hexanethiol (11.8 g, 0.1 mol) yielded 80% (19 g, 0.08 mol) of the pure disulfide: bp 228 °C/701 mmHg; ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20–1.45 (m, 6H), 1.60–1.75 (m, 2H), 2.60–2.70 (t, 2H, J = 7.5 Hz); EI^+ (GC/MS, VG-70) *m/z* 234.1 (M^+), 149.9, 117.0, 85.1, 55.0, 43.0; IR (vapor phase) ν 2935, 2860, 1461, 1348, 1288, 731 cm^{-1}. Anal. Calcd for $C_{12}H_{26}S_2$: C, 61.47; H, 11.18. Found: C, 61.19; H, 11.03.

***tert*-Butyl hexyl disulfide** was prepared according to the standard procedure.[18] 1-Bromohexane (16.5 g, 0.1 mol), excess $Na_2S_2O_3$, and *tert*-butanethiol (9 g, 0.1 mol) yielded 80% (16 g, 0.08 mol) of the pure disulfide: bp 152 °C/20 mmHg; ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20–1.45 (m, 15H), 1.55–1.65 (m, 2H), 2.60–2.70 (t, 2H, J = 7.5 Hz); EI^+ (GC/MS, VG-70) *m/z* 206 (M^+), 150, 117, 85, 79, 57; IR (vapor phase) ν 2935, 2872, 1463, 1367, 1288, 1167 cm^{-1}. Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74. Found: C, 58.15; H, 10.65.

***tert*-Butyl 2-octyl disulfide** was prepared from *tert*-butanethiol and 2-octanethiol according to the literature procedure.[20,21] 2-Octanethiol was prepared from a mixture of 2-bromooctane (77.2 g, 0.4 mol) and thiourea (10.1 g, 0.5 mol), followed by hydrolysis with excess sodium hydroxide.[20] A 1:1 mixture of 2-octanethiol and *tert*-butyl thiol was oxidized with I_2.[20,21] The pure disulfide was isolated in a 30% yield from the mixture of disulfides by fractional distillation: bp 177 °C/90 mmHg; ^1H NMR (200 MHz, $DCCl_3$): δ 0.90 (t, 6H, J = 7 Hz), 1.20–1.70 (m, 22H), 2.70–2.80 (m, 1H); EI^+ (GC/MS, VG-70) *m/z* 234.2 (M^+), 178.2, 146.1, 113.1, 71.1, 57.0, 41.0; IR (vapor phase) ν 2934, 2871, 1460, 1368, 1165, 1017 cm^{-1}. Anal. Calcd for $C_{12}H_{26}S_2$ *m/z* 234.14894, found 234.14760.

Di-2-octyl disulfide was prepared by the I_2 oxidation of 2-octanethiol (10 g, 0.07 mol).[20] The product was isolated in a 50% yield (10.1 g, 0.035 mol): bp 198–200 °C/90 mmHg; ^1H NMR (200 MHz, $DCCl_3$) δ 0.90 (t, 6H, J = 7 Hz), 1.20–1.70 (m, 26H), 2.70–2.82 (m, 2H); EI^+ (GC/MS, VG-70) *m/z* 290 (M^+), 178, 113, 71, 57, 41; IR (vapor phase) ν 2934, 2868, 1460, 1378, 1271, 1015 cm^{-1}. Anal. Calcd for $C_{16}H_{34}S_2$: C, 66.13; H, 11.79. Found: C, 66.10; H, 11.91.

1-Hexyl cyclohexyl disulfide was prepared according to the standard procedure.[18] 1-Bromohexane (16.5 g, 0.1 mol), excess $Na_2S_2O_3$, and cyclohexanethiol (11.6 g, 0.1 mol) were used in the reaction. The product was isolated in 75% yield (17 g, 0.075 mol): bp 205–207 °C/701 mmHg; ^1H NMR (200 MHz, $DCCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.20–1.40 (m, 12H), 1.55–1.85 (m, 4H), 1.90–2.10 (m, 2H), 2.50–2.60 (m, 1H), 2.70 (t, 2H, J = 7.5 Hz); EI^+ (GC/MS, VG-70) *m/z* 232.0 (M^+), 150.1, 117.1, 83.1, 55.0; IR (vapor phase) ν 2939, 2865, 1453, 1343, 1264, 1199, 994, 887 cm^{-1}. Anal. Calcd for $C_{12}H_{24}S_2$: C, 62.01; H, 10.41. Found: C, 61.70; H, 10.80.

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