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The Reaction of Dibutyl Disulfide with Hydrogen Atom

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The title reaction was investigated at room temperature and under pressures ranging from 133 to 2660 Pa. 1-Butanethiol, butane, and 1-butene were the main products. In the reaction with deuterium atom, dibutyl disulfide and 1-butanethiol were not deuterated, while butane was monodeuterated. The following mechanism was proposed to account for the product composition and its pressure dependency as well as the deuterium labeling of the products. $C_4H_9SSC_4H_9+D\cdot \rightarrow n\text{-}C_4H_9SD + n\text{-}C_4H_9S\cdot$, $n\text{-}C_4H_9S\cdot + D\cdot \rightarrow n\text{-}C_4H_9SD^*$, $n\text{-}C_4H_9SD^* + M \rightarrow n\text{-}C_4H_9SD$, $n\text{-}C_4H_9SD^* \rightarrow \Delta'\text{-}C_4H_8 + HDS$, $n\text{-}C_4H_9SD^* \rightarrow n\text{-}C_4H_9\cdot + DS\cdot$, $n\text{-}C_4H_9\cdot + D\cdot \rightarrow n\text{-}C_4H_9D$, $n\text{-}C_4H_9\cdot + D\cdot \rightarrow \Delta'\text{-}C_4H_8 + HD$.

In our continuing effort to work out the mechanism of the reactions between thiols with H atom,[1-3] involvement of chemically activated thiols and metastable intermediate containing trivalent sulfur has been pointed out as its characteristic feature. The overall reaction is the hydrodesulfurization of thiols, which is initiated by

$$RSH + H\cdot \rightarrow RS\cdot + H_2 \tag{1}$$

and

$$RSH + H\cdot \rightarrow R\cdot + H_2S \tag{2}$$

taking place simultaneously. Thiyl radical, produced in reaction (1), subsequently forms chemically activated thiol, RSH*, which in turn becomes a source of the unique hydrodesulfurization. Reaction (2), a novel metathesis characteristic to the reactions of sulfur containing compounds with H atom, is considered to take place via the formation of metastable intermediate, $RSH_2\cdot$. Product composition of the overall reaction is governed by the relative importance between reactions (1) and (2).

In the present work, the study is extended to the reactions of disulfide with H and D atoms. Dibutyl disulfide is chosen as the substrate. The present experimental results can thus be compared conveniently with those of 1-butanethiol already accumulated in our laboratory.[1] As a result of the present study, mechanistic interpretation of reaction pathway turns out to be much less equivocal with this particular substrate, since it does not directly produce R· as in reaction (2).

Experimental

A conventional discharge flow apparatus was adopted. Details were described elsewhere.[1] Dibutyl disulfide and H_2 (or D_2), both diluted with excess He, were introduced into a Pyrex reactor tube of 400 mm in length and 27 mm in inside diameter. Flow rates of dibutyl disulfide, H_2 (or D_2), and He were 0.001 ml(NTP) s^{-1}, 0.01 ml(NTP) s^{-1}, and 0.72—14.4 ml(NTP) s^{-1} respectively. H atom (or D atom) was generated by passing H_2 (or D_2) through a microwave discharge cavity placed at the upstream side of the reactor. The reactor surface was coated with boric acid to prevent H atom (or D atom) from recombination.

The reaction was carried out at room temperature and under pressures ranging from 133 to 2660 Pa. Reacting gas mixture was intermittently withdrawn through a nozzle and was isolated into a side arm chilled by liquid N_2. The isolated sample was then analyzed by GC and GC-MS, using VZ-10 column (2 m, 328 K) for hydrocarbons and polyethylene glycol column (1 m, 363 K) for organosulfur compounds.

Commercially available purest grade dibutyl disulfide was purified by trap-to-trap distillation, and the fraction of better than 99% purity was used. Cylindered gases of H_2, D_2, and He were dried by passing through a train of liquid N_2 traps.

Results

1-Butanethiol, butane, and 1-butene were the main products of the reaction with H atom. Small amounts of *cis*-2-butene, *trans*-2-butene, and fragmental products such as propane, propylene, ethane, and ethylene were also formed. No sulfide was detected in the product. Based on the mass balance, methane, if any, was formed only in a limited amount.

Product composition vs. conversion relations observed with the three major products under 133, 530, and 2660 Pa are shown in Figs. 1, 2, and 3, respectively. Although 1-butanethiol was by far the most important, all the three major components were clearly the

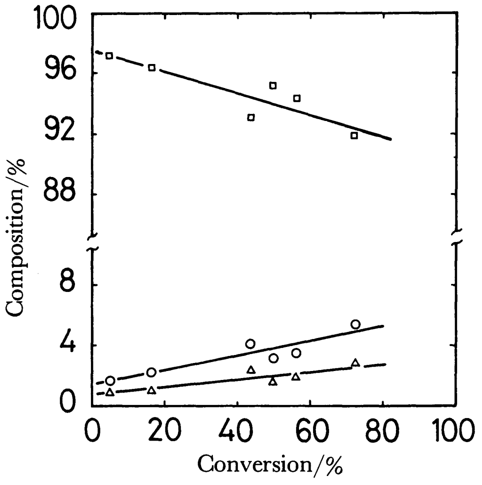

Fig. 1. Composition vs. conversion relation under 133 Pa. □: 1-Butanethiol, ○: butane, △: 1-butene.

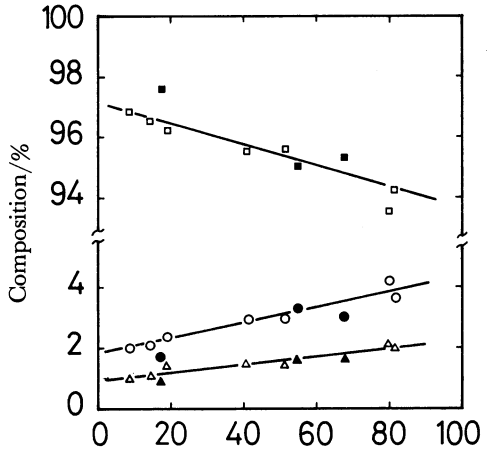

Fig. 2. Composition vs. conversion relation under 530 Pa. □: 1-Butanethiol, ○: butane, △: 1-butene. Filled symbols indicate the reaction with D atom.

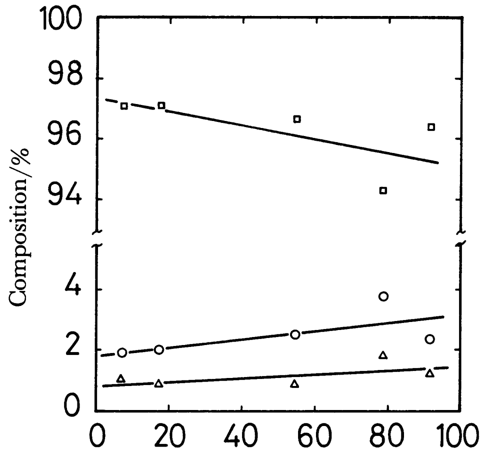

Fig. 3. Composition vs. conversion relation under 2660 Pa. □: 1-Butanethiol, ○: butane, △: 1-butene.

initial products. And, up to 90% conversion, these three together accounted practically for all the substrate consumed. As can be seen with filled symbols in Fig. 2, the product composition remained unchanged when D atom was used instead of H atom. The decreasing trend in 1-butanethiol compensated the increasing trend in butane and 1-butene. Thus, the reaction can be described by the following stoichiometry:

$$(C_4H_9S)_2 + H \rightarrow (2-a-b)\ C_4H_9SH + a\ C_4H_{10} + b\ C_4H_8$$

where a and b are stoichiometric coefficients. Irrespective of the pressure used, the ratio a/b of about 0.5 was deduced from the figures. The ratio $(a+b)/(2-a-b)$, however, decreased as the pressure increased. The latter ratios were 0.08 at 133 Pa, 0.05 at 530 Pa, and 0.03 at 2660 Pa.

Practically no isotopic mixing was observed with dibutyl disulfide left unreacted. Deuterium distributions observed with butane and 1-butene are listed in Table 1 for a few different conversions. Approximately one D atom was introduced into each butane molecule produced. Both 1-butene[D_0] and 1-butene-[D_1] were formed, and the latter became progressively important as conversion increased.

Table 1. Relative Abundance of Deuterium Labeled Products

Conversion/%	Butane			1-Butene		
	D_0	D_1	D_2	D_0	D_1	D_2
16.8	9	100	1	100	27	1
46.6	2	100		100	71	1
68.1		100		100	116	
89.1	3	100	2	100	103	2

The conventional GC-MS analysis showed no D-labeled 1-butanethiol. But, with a quadrapole mass spectrometer connected directly to the reactor tube, 1-butanethiol[D_1] was found to be an exclusive constituent. It may therefore be concluded that 1-butanethiol was monodeuterated in the course of the reaction, and that the result as observed with GC-MS was due to the retro H-D exchange between residual water in the ionization chamber and mercapto-D of 1-butanethiol[D_1].

Discussion

Heat of Formation of the Species in Relevance with the Present System. The values of the heat of formation of the species involved in the present study are estimated using a conventional additivity rule,[4] and are listed in Table 2. Error limits of the listed values are ±1.0 kcal mol^{-1} (1 kcal$_{th}$=4.184 kJ) for stable molecules, and ±2.0 kcal mol^{-1} for radicals. The reliability level of the additivity rule used here may be seen by comparing the tabulated data with literature values of $\Delta H^0_f(C_4H_9SH)=-21.06$ kcal mol^{-1},[5] and $\Delta H^0_f(C_4H_9SSC_4H_9)=-37.63$ kcal mol^{-1}.[6]

Initial Step. In analogy with the reactions of thiols and sulfides with H atom, and based on the fact that fragmentation of alkyl group was only trivial, the initial act of H atom is presumably its addition to one of the S atoms of the substrate molecule. Therefore, the following reactions are plausible.

$$C_4H_9SSC_4H_9 + D\cdot \rightarrow n\text{-}C_4H_9SD + C_4H_9S\cdot \qquad (3)$$

$$C_4H_9SSC_4H_9 + D\cdot \rightarrow n\text{-}C_4H_9SSD + C_4H_9\cdot \qquad (4)$$

For the sake of clarity, we hereafter write D standing for both hydrogen and deuterium atoms. Based on the

Table 2. Standard Heat of Formation of the Related Species[a)]

Species	ΔH^0_f
	kcal mol^{-1}
n-C_4H_9SH	−21.1
n-C_4H_9SSH	−16.8
$C_4H_9SSC_4H_9$	−37.3
n-$C_4H_9\cdot$	15.8
n-$C_4H_9S\cdot$	17.8

a) Ref. 4.

values listed in Table 2, reactions (3) and (4) are exothermic by 18.1 and 15.8 kcal mol^{-1}, respectively. Therefore, reaction (3) is thermochemically more favorable.

We may also reject reaction (4) as a reaction of importance on the ground of the following argument. If reaction (4) takes place significantly, butyl radical should subsequently form butane and butenes through the intermolecular H transfer or else should form sulfide through the following reaction:

$$C_4H_9\cdot + C_4H_9SSC_4H_9 \rightarrow C_4H_9SC_4H_9 + C_4H_9S\cdot. \quad (5)$$

The results observed, however, turned out to be contrary to the above presumption. As will be described later, small amount of hydrocarbons observed in the product can be simply accounted for by the secondary reactions of $C_4H_9S\cdot$ produced in reaction (3). And, dibutyl sulfide, expected product of reaction (5), was not detected in the product.

The initiation quite analogous to reaction (3) was also suggested in the reactions of dimethyl and diethyl disulfides with H atom.[7] The reaction is considered to take place via the intermediary formation of the novel adduct $C_4H_9SS(H)C_4H_9$.[2] However, to date, no mention has been made on the structure and stability of such adduct. Recently, it was proposed that S-S bond in $RSS(R)SR\cdot$, formed in the reaction between $RS\cdot$ and RSSR, was weakened by at least one quarter of a normal S-S *sigma*-bond.[8]

Secondary Reactions. In their study on the reactions of dimethyl and diethyl disulfides with H atom, Strausz et al. reported the formation of a considerable amount of polymers.[7] The formation of polymers in the above instance, being due to the low concentration of H atom used in their work, made it difficult for them to elucidate the fate of thiyl radical produced by reaction (3). In the present work, H atom concentration was maintained at the level not less than the concentration of the substrate. Consequently, practically no polymer was formed, and the amount of 1-butanethiol in the product accounted for more than 90% of dibutyl disulfide consumed over the wide conversion range. This indicates that reaction (3) is followed by

$$C_4H_9S\cdot + D\cdot \rightarrow n\text{-}C_4H_9SD^* \quad (6)$$

and

$$n\text{-}C_4H_9SD^* + M \rightarrow n\text{-}C_4H_9SD, \quad (7)$$

and that dibutyl disulfide is considerably more reactive than 1-butanethiol in the reaction with H atom. The latter statement is in accord with some existing rate data listed in Table 3. Further reactions of 1-butanethiol may therefore be ignored in formulating a group of secondary reactions. It should be noted here that the asterisk denotes chemically activated species and M the bath molecule.

Conceivable reactions of the chemically activated 1-butanethiol, other than reaction (7), are

$$n\text{-}C_4H_9SD^* \rightarrow \Delta'\text{-}C_4H_8 + HDS \quad (8)$$

and

$$n\text{-}C_4H_9SD^* \rightarrow n\text{-}C_4H_9\cdot + DS\cdot. \quad (9)$$

Reactions subsequent to reaction (9) are the following:

$$n\text{-}C_4H_9\cdot + D\cdot \rightarrow n\text{-}C_4H_9D \quad (10)$$

and

$$n\text{-}C_4H_9\cdot + D\cdot \rightarrow \Delta'\text{-}C_4H_8 + HD. \quad (11)$$

According to the scheme, consisting of reactions (7)—(11), [hydrocarbon]/[1-butanethiol] ratio should decrease as pressure increases. This is quite in accord with the result mentioned earlier that the ratio $(a+b)/(2-a-b)$ decreased from 0.08 at 133 Pa to 0.03 at 2660 Pa. One D atom is introduced into butane through reaction (10), while no channel exists to produce D-labeled 1-butene. During a later stage, however, D-labeled 1-butene may be formed through the sequence comprising D-addition and H-abstraction. These are also quite in accord with the present result.

It should be noted that the sequence of elementary reactions, from reaction (6) through reaction (11), is identical with the one proposed for the reaction of 1-butanethiol with H atom, and was, therefore, thoroughly discussed already.[1,3]

1-Butene/Butane Ratio. According to the proposed mechanism, the following formula can be obtained to relate the ratio of 1-butene to butane.

$$[\text{1-butene}]/[\text{butane}] = k_8/k_9 + k_{11}/k_{10}(1 + k_8/k_9).$$

The ratio [1-butene]/[butane] was observed to be 0.5 in the present study. The ratio k_{11}/k_{10}=0.05 was estimated in the reactions of ethyl radical with H atom[10] and propyl radical with methyl radical.[11] Based on

Table 3. Rate Constant and Activation Energy of the Reaction of Sulfur Compounds with H Atom

Compound	Rate constant	Activation energy	Reference
	$l\,mol^{-1}\,s^{-1}$	kcal mol^{-1}	
Dimethyl disulfide	4.80×10^9	0.1	7
Diethyl disulfide	2.74×10^9	1.7	7
Dimethyl sulfide	2.10×10^8	2.6	9
Diethyl sulfide	0.80×10^8	3.8	9
Thiolane	2.92×10^8	2.0	3
Methanethiol	7.80×10^8	1.7[a], 2.6[b]	2
1-Butanethiol	1.01×10^8	2.2[a], 3.2[b]	1

a) Assigned for reaction (1). b) Assigned for reaction (2).

these values, the value of 0.43 can be deduced for the ratio k_8/k_9. On the other hand, $k_8/k_9=0.18$ was reported in the very low pressure pyrolysis of 1-butanethiol.12) There is, therefore, a considerable difference between the chemically activated 1-butanethiol and the thermo-energized 1-butanethiol in their H-addition and H-abstraction rate ratios.

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