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Pressure Dependence of the Reaction of Thiolane with H and D Atom

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The title reaction was investigated at room temperature and under pressures ranging from 133 to 2660 Pa, using a conventional discharge flow reactor. 1-Butanethiol, butane, and 1-butene were the main products, whose compositions varied according to the pressure. In the reaction with deuterium atom, 1-butene was monodeuterated, while 1-butanethiol and butane were dideuterated. The following mechanism was proposed to account for the product compositions and their pressure dependencies as well as the deuterium labeling of the products.

$$\begin{aligned}
(CH_2)_4S + H &\longrightarrow CH_2(CH_2)_3SH && (1)\\
CH_2(CH_2)_3SH + H &\longrightarrow CH_3CH_2CH_2CH_2SH^* && (2)\\
CH_3CH_2CH_2CH_2SH^* &\longrightarrow CH_3CH_2CH_2CH_2SH && (3)\\
&\longrightarrow CH_3CH_2CHCH_2 + H_2S && (4)\\
&\longrightarrow CH_3CH_2CH_2CH_2 + HS && (5)\\
CH_3CH_2CH_2CH_2 + H &\longrightarrow CH_3CH_2CHCH_2 + H_2 && (6)\\
&\longrightarrow CH_3CH_2CH_2CH_3 && (7)
\end{aligned}$$

In the comparatively few mechanistic studies, the common initial step being characteristic of direct attack on sulfur has been proposed for the reactions of hydrogen atom with cyclic sulfides. The subsequent decomposition paths of trivalent sulfur complexes so formed, however, were quite different from each other. With the thiirane$^{1)}$ and thietane$^{2)}$ the concerted decomposition mechanisms were proposed as

$$\begin{aligned}
(CH_2)_2S + H &\longrightarrow CH_2CH_2 + SH\\
(CH_2)_3S + H &\longrightarrow CH_3CHCH_2 + SH.
\end{aligned}$$

With thiolane, to account for the predominant formation of 1-butanethiol, the distinct C–S bond cleavage and subsequent reactions, Reactions 1—4, were proposed in our previous study$^{3)}$

$$\begin{aligned}
(CH_2)_4S + H &\longrightarrow CH_2(CH_2)_3SH && (1)\\
CH_2(CH_2)_3SH + H &\longrightarrow CH_3CH_2CH_2CH_2SH^* && (2)\\
CH_3CH_2CH_2CH_2SH^* &\longrightarrow CH_3CH_2CH_2CH_2SH && (3)\\
&\longrightarrow CH_3CH_2CHCH_2 + H_2S. && (4)
\end{aligned}$$

An asterisk denotes a vibrational energized species. Reaction 4, a molecular H_2S elimination channel for the decomposition of chemically activated 1-butanethiol, was tentatively proposed on the analogue to the decomposition of alkyl halide or aliphatic alcohol to interpret the formation of 1-butene, one of the hydrocarbon products. Butane, another hydrocarbon product, was interpreted to be produced via secondary reactions of 1-butanethiol and 1-butene.

In very little studies up to date of our study on 1-butanethiol, thermal reactions of thiols have been reported to proceed either by a free radical chain mechanism or by a molecular H_2S elimination mechanism, neither of which have conclusive evidence for the validity.$^{4,5)}$ Recently, we have studied the thermal decomposition of 1-butanethiol, using low pressure pyrolysis technique combined with deuterium labeling method, and reached the conclusion that the decomposition is through two parallel channels, Reactions 4′ and 5′$^{5)}$

$$\begin{aligned}
CH_3CH_2CH_2CH_2SH &\longrightarrow CH_3CH_2CHCH_2 + H_2S && (4')\\
CH_3CH_2CH_2CH_2SH &\longrightarrow CH_3CH_2CH_2CH_2 + HS. && (5')
\end{aligned}$$

On the other hand, we have studied the reaction of dibutyl disulfide with hydrogen atom,$^{6)}$ and found that we have to propose another parallel decomposition channel to Reaction 4, Reaction 5

$$CH_3CH_2CH_2CH_2SH^* \longrightarrow CH_3CH_2CH_2CH_2 + HS \qquad (5)$$

of chemically activated 1-butanethiol formed in the reaction to give a satisfactory explanation on the product compositions and their pressure dependencies as well as deuterium distributions in the products. Reactions 4 and 5 were also shown to be flexible in giving an explanation of reaction of 1-butanethiol with hydrogen atom,$^{7)}$ where chemically activated 1-butanethiol was also considered to be formed.

These facts aroused our attempt to reinvestigate the reaction of thiolane with hydrogen (and deuterium) atom over a wide pressure range for acquiring a clearer picture of the chemically activated species in this reaction.

Experimental

The adopted apparatus and procedure were similar to those described in our previous work.$^{3)}$ In brief, the apparatus consisted of discharge flow reactor, reactant vaporizer, liq. N_2 chilling traps for trapping product, flow control line, and evacuation system. Thiolane and H_2 (or D_2), both diluted in excess of He, were introduced into a Pyrex reactor of 400 mm in length and 27 mm in inside diameter. Flow rate of thiolane, 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. Hydrogen atom (or deuterium atom) was generated by passing H_2 (or D_2) through a microwave cavity at upstream side of reactor. To prevent hydrogen atom (or deuterium atom) from recombination, the reactor surface was coated with boric acid.

The reaction was carried out at room temperature and under pressures ranging from 133 to 2660 Pa. Many attempts were made to get observation at low conversions. Reaction gas mixture was intermittently withdrawn through a nozzle and was isolated into an arm chilled by liq. N_2. The isolated sample was then analyzed by gas chromatography (GC) and gas chromatograph-mass spectrometer (GC-MS), using VZ-10 column (2 m, 55 °C) for hydrocarbons and polyethylene glycol (3 m, 80 °C) for organosulfur compounds.

Commercially available purest grade thiolane was purified by trap-to-trap distillation, and the middle one third 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 liq. N_2 traps.

Results

Course of reaction was followed up to conversion of 60%. Product composition vs. conversion relations observed 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 including 1-butene and butane were evidently the initial products. The adequacy of interpretation that butane was an initial product will be presented in detail later in discussion. Small amounts of fragmental products such as propane, propylene, ethane, and ethylene were also formed. However, they all decreased to a negligible amount as pressure increased.

When deuterium atom was used instead of

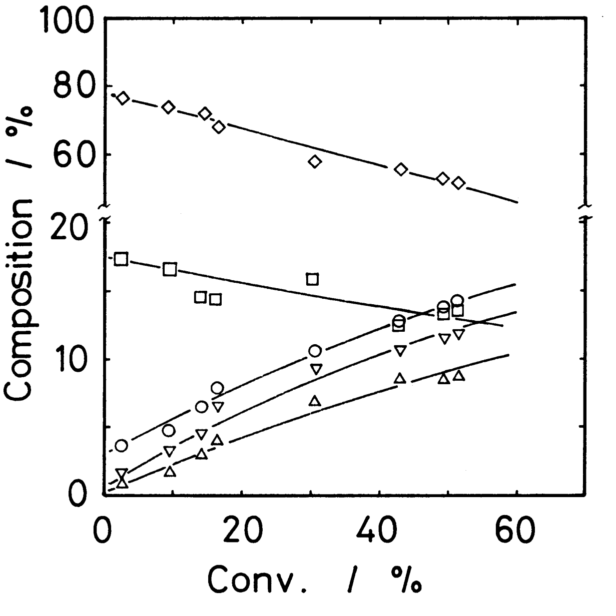

Fig. 1. Composition vs. conversion relation under 133 Pa.
◇: 1-Butanethiol, ○: butane, □: 1-butene, △: C_2 hydrocarbons, ▽: C_3 hydrocarbons.

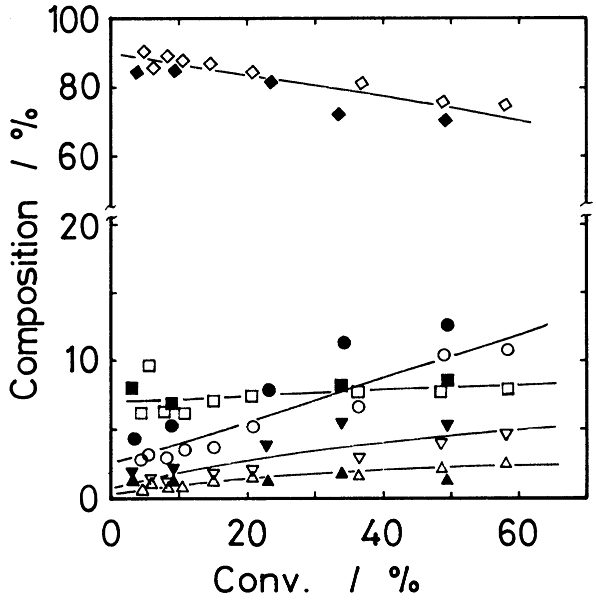

Fig. 2. Composition vs. conversion relation under 530 Pa.
◇: 1-Butanethiol, ○: butane, □: 1-butene, △: C_2 hydrocarbons, ▽: C_3 hydrocarbons.
(Filled points denote reaction with deuterium atom.)

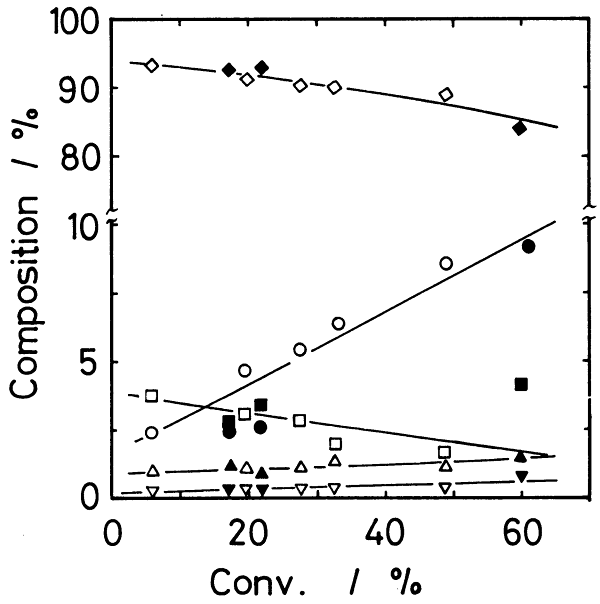

Fig. 3. Composition vs. conversion relation under 2660 Pa.
◇: 1-Butanethiol, ○: butane, □: 1-butene, △: C_2 hydrocarbons, ▽: C_3 hydrocarbons.
(Filled points denote reaction with deuterium atom.)

hydrogen atom, quite similar results were obtained with respect to the composition-conversion behavior as shown in Figs. 2 and 3 by filled points. Practically no isotopic mixing was observed with thiolane left unreacted in the reaction with deuterium atom. Deuterium distributions observed with butane and 1-butene are listed in Table 1 for a few different conversions. Two deuterium atoms were introduced into each butane molecule produced, and one into each 1-butene. 1-Butene[D_2] and butane[D_3] were observed as progressively important with the increase of conversion. The GC-MS analysis also showed that only one deuterium atom was introduced into each 1-butanethiol molecule produced.

Both butane/1-butanethiol and 1-butene/1-butanethiol ratios tend to increase linearly as the conversion increases. The trend is illustrated in Fig. 4. The values of 0.020, 0.016, 0.006 for butane/1-butanethiol, and of 0.239, 0.077, 0.029 for 1-butene/1-butanethiol at 133, 530, 2660 Pa were obtained when extrapolating the ratios at various pressures to zero conversion. Clearly these values exhibit certain pressure dependencies of the initial product compositions.

Table 1. Deuterium Distribution in Butane and 1-Butene

Press.	Conv.	Butane			1-Butene		
Pa	%	d_1	d_2	d_3	d_0	d_1	d_2
530	2.0	0	100	0	0	100	7
530	3.0	0	100	12	1	100	12
133	6.5	14	100	11	0	100	7
2660	10.7	15	100	9	4	100	18
530	12.1	10	100	26	3	100	20
530	30.3	10	100	33	9	100	22
2660	43.5	14	100	22	3	100	20

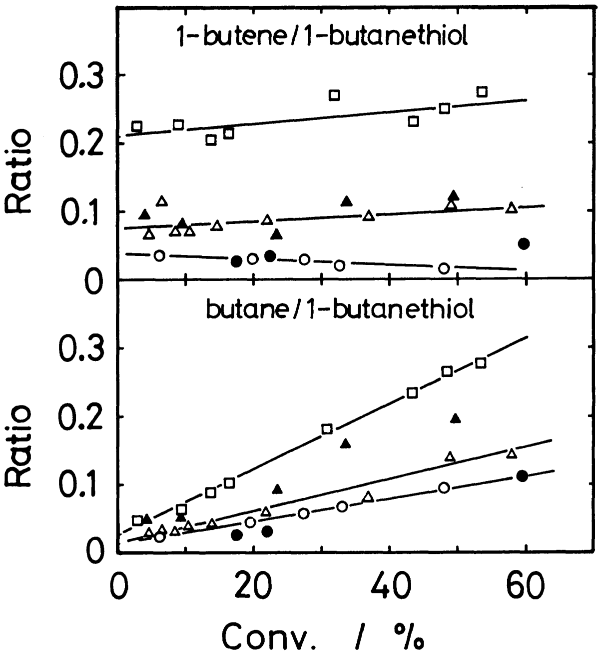

Fig. 4. Amounts of 1-butene and butane relative to 1-butanethiol.
□: 133 Pa, △: 530 Pa, ○: 2660 Pa.
(Filled points denote reaction with deuterium atom.)

Discussion

Primary Reaction. The fact that no isotopic mixing was observed with thiolane left unreacted in the reaction with deuterium atom eliminated the possibility of hydrogen abstraction-addition on ring. This approved the characteristic hydrogen atom attack on sulfur proposed previously to be valid. Thus the Reactions 1—4 proposed previously kept their validity for reasons that they give a proper interpretation of primary formations of 1-butanethiol and 1-butene.[3] However, butane is not referred to in Reactions 1—4. In fact, butane was shown not to be formed from the reactions of 1-butene and 1-butanethiol with hydrogen atom, the conclusive diagnosis of which will be presented in the discussion on secondary reaction later. Thus, to interpret the primary formation of butane, we add Reaction 5, a parallel decomposition channel to Reaction 4 for chemically activated 1-butanethiol, and subsequent Reactions 6 and 7. The reaction formulas 1—7 should be written as follows,

$$\begin{array}{rll}
(CH_2)_4S + D & \longrightarrow CH_2(CH_2)_3SD & (1) \\
CH_2(CH_2)_3SD + D & \longrightarrow CH_2DCH_2CH_2CH_2SD^* & (2) \\
CH_2DCH_2CH_2CH_2SD^* & \longrightarrow CH_2DCH_2CH_2CH_2SD & (3) \\
 & \longrightarrow CH_2DCH_2CHCH_2 + HDS & (4) \\
 & \longrightarrow CH_2DCH_2CH_2CH_2 + DS & (5) \\
CH_2DCH_2CH_2CH_2 + D & \longrightarrow CH_2DCH_2CHCH_2 + HD & (6) \\
 & \longrightarrow CH_2DCH_2CH_2CH_2D. & (7)
\end{array}$$

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

According to this scheme, 1-butene[D_1], butane[D_2], and 1-butanethiol[D_2] should be given when deuterium atom was used. The initial deuterium distribution of 1-butene and butane was in conformity with this inference, while the GC-MS observation on 1-butanethiol was apparently inconsistent with this inference. However, by a contrast analysis of the separately prepared 1-butanethiol[S-D] using a direct sampling quadrupole mass spectrometer, we verified that, even if the mercapto-hydrogen is deuterated perfectly, conventional GC-MS analysis can not give any evidence about the mercapto-deuterium due to the retro H–D exchange with residual water in the column and in the ionization chamber. It may therefore be concluded that 1-butanethiol was actually dideuterated in the course of reaction, and that the

Table 2. Rate Constants and Activation Energy of the Reactions of Related Species with Hydrogen Atom

Reactant		log A	E_a / kJ mol^{-1}	Rate constant at 300 K / cm^3 mol^{-1} s^{-1}	Ref.
Thiolane		9.93	8.4	2.92*10^{11}	3
1-Butanethiol	(a)	9.20	9.3	3.84*10^{10}	3
	(b)	10.11	13.3	6.27*10^{10}	3
1-Butene		13.17	6.2	1.32*10^{12}	10
Butane		13.3—14.4	6.7—8.5	ca. 2*10^8	11

(a): for Reaction 8. (b): for Reaction 9.

result as observed with GC-MS just should be interpreted as monodeuteration of butyl group of 1-butanethiol.

The Reactions 6 and 7 are the well-known disproportionation and recombination reactions for an alkyl radical with hydrogen atom. From the reported values for the reactions of ethyl radical with hydrogen atom[8] and of propyl radical with methyl radical,[9] we can reasonably estimate the k_6/k_7 to be about 0.05. Thus, the predominant source of 1-butene was plausibly molecular H_2S elimination of chemically activated 1-butanethiol, Reaction 4, rather than Reaction 6.

Secondary Reaction. Table 2 shows rate constants of some related species with hydrogen atom at room temperature. Thiolane, 1-butanethiol, and 1-butene all have a much higher reactivity over butane toward hydrogen atom. We may therefore ignore the reaction of butane with hydrogen atom in formulating a group of secondary reactions.

Conceivable reactions of 1-butanethiol with hydrogen atom can be cited from our study[7] on the reaction of 1-butanethiol with hydrogen atom as follows

$$\mathrm{CH_2DCH_2CH_2CH_2SD} + \mathrm{D}$$
$$\longrightarrow \mathrm{CH_2DCH_2CH_2CH_2S} + \mathrm{D_2} \quad (8)$$
$$\longrightarrow \mathrm{CH_2DCH_2CH_2CH_2} + \mathrm{D_2S}. \quad (9)$$

Reactions subsequent to Reaction 8 are

$$\mathrm{CH_2DCH_2CH_2CH_2S} + \mathrm{D}$$
$$\longrightarrow \mathrm{CH_2DCH_2CH_2CH_2SD^*} \quad (10)$$

and Reactions 3—5. Reactions subsequent to Reaction 9 are Reactions 6 and 7. For 1-butene, the secondary reaction with hydrogen atom is the well-known addition to double bond giving butyl and *s*-butyl radicals. The reactions of these radicals with hydrogen atom result in the formation of butane, 2-butenes, and regeneration of 1-butene.

The decreases of the composition of 1-butanethiol and 1-butene with the increase of conversion shown in Figs. 1, 2, and 3 indicate the secondary reactions of 1-butanethiol and 1-butene with hydrogen atom. Moreover, from Fig. 4, the almost fixed 1-butene/1-butanethiol ratio relative to the conversion exhibits the similar reactivity toward hydrogen atom of both. This fact is also in quite accord with the reported rate constant data listed in Table 2. As a net result of secondary reactions of 1-butene and 1-butanethiol, butane/1-butanethiol solely increased with the increase of conversion, as shown in Fig. 4.

Table 3. Comparison of k_4/k_5 Ratios of 1-Butanethiol

Reaction	k_4/k_5	Energized level / kJ mol^{-1}	Ref.
Thermal decomposition	0.18	310$^{a)}$	5
Dibutyl disulfide+H	0.43	385$^{b)}$	6
Thiolane+H	3.0—9.7	410$^{c)}$	This work

a) Calculated by E_0+RT, E_0 is activation energy; b) bond dissociation energy of S-H bond; c) bond dissociation energy of primary C-H bond.

On account of secondary reaction, one may predict the change of deuterium distribution in products when deuterium atom was used. Secondary reaction of 1-butanethiol can not introduce any additional deuterium into 1-butene, butane, and itself, while the secondary reaction of 1-butene introduces two more deuterium atoms into butane, one more into 1-butene, leading to the formation of butane[D_3] and 1-butene[D_2]. Table 1 shows that the abundances of butane[D_3] and 1-butene[D_2] increased as conversion increased, and the both approached to zero at low conversion. The latter fact makes primary formation of butane evident, because 1-butanethiol is known to be never more reactive toward hydrogen atom than 1-butene.

Pressure Dependence of Primary Products and Decomposition of Chemically Activated 1-Butanethiol. The pressure dependence of the initial proportion of 1-butene gives an undoubted evidence for the formation of chemically activited 1-butanethiol in this reaction. The initial proportion of butane was so small that its pressure dependence was submerged into experimental error. Therefore we can not say any about its pressure dependency arbitrarily, but we can conclude that the chemically activated 1-butanethiol formed in this reaction has a higher selectivity to the concerted channel of 4 over 5.

According to the proposed reaction mechanism, the following formula may be deduced to relate the initial products composition with k_4/k_5.

$$\frac{[\text{1-butene/1-butanethiol}]}{[\text{butane/1-butanethiol}]} = \frac{k_6}{k_7} + \frac{k_4}{k_5}\left(1+\frac{k_6}{k_7}\right)$$

Table 3 listed the evaluated values of k_4/k_5 for thermal decomposition of 1-butanethiol and decomposition of chemically activated 1-butanethiol created from different reactions. A comparison can be made between the values of k_4/k_5 and the energized level of

1-butanethiol. The relevancy between the two may give a rough explanation of the difference in the values of k_4/k_5.

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