Studies of Fragment Ion Distribution and Reaction by the Use of a Charge Spectrometer. VII. Fragmentation of Aliphatic Thiol Ions Produced by Charge Exchange with Positive Ions

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Fragmentation of molecular ions of methanethiol, ethanethiol, two kinds of propanethiols, and four kinds of butanethiols formed by charge exchange with positive ions has been studied using a tandem mass spectrometer. The results are compared with those of the corresponding alcohols obtained by Lindholm and coworkers, and similarities and differences between both series of ions are pointed out. The effect of the structure of the molecule on fragmentation is discussed. The fragment ions derived from primary scission are predicted on the basis of the EHMO calculation.

No report has yet been published on fragmentation of thiol ions formed by charge exchange with positive ions, whereas the phenomena were intensively studied with alcohols by Lindholm and coworkers.[1–4] We have been interested in the breakdown phenomena of methanol[5] and methylamine[6] after charge exchange. It is an important problem to understand what mechanisms are involved in the fragmentation of a series of compounds RX, where R is an alkyl group and X is a substituent. Although it would be interesting to elucidate the fragmentation processes of these compounds, previous authors have not studied them systematically. The effects of the size and structure of R, for example, have not been well understood so far.

In this report we have studied fragmentation mechanisms in a series of alkyl thiol ions, RSH^+, formed by charge exchange with positive ions, and found somewhat different behavior between thiols and alcohols. In the studies of electron impact mass spectroscopy, similarities between both series of compounds are usually emphasized, though the abundance of the parent peaks is different.[7] The differences of behavior of the fragmentation between both series of compounds have been made clear by observations using charge exchange reactions, where the energy transfered to the molecular ions is well defined.

Experimental

All the reagents, guaranteed by gas chromatographic analysis, were purchased from the Tokyo Kasei Co. Their purities were re-checked by gas chromatograph before use. The reagents were as follows: methanethiol CH_3SH, ethanethiol C_2H_5SH, 1-propanethiol $CH_3(CH_2)_2SH$, 2-propanethiol $CH_3CH(SH)CH_3$, 1-butanethiol $CH_3(CH_2)_3SH$, 2-methyl-1-propanethiol $(CH_3)_2CHCH_2SH$, 1-methyl-1-propanethiol $CH_3CH_2CH(SH)CH_3$, and 2-methyl-2-propanethiol $(CH_3)_3C$-SH.

Primary ions for the charge exchange reactions were $C_6H_6^+$, H_2S^+, $C_2H_2^+$, Xe^+, Kr^+, Ar^+, Xc^{2+}, Kr^{2+}, Ne^+, Ar^{2+}, and He^+; the source materials were of the high purity reported in the previous studies.[5,6,8–10]

A tandem mass spectrometer of the perpendicular type used here was described in the previous report.[11]

The pressure of the reaction chamber was kept below 6×10^{-6} Torr to avoid secondary reactions with other molecules.

Results

Methanethiol: The appearance potential of methanethiol is 9.44 eV,[12] and the parent ion is produced by the elimination of one of the lone-pair electrons located at the sulfur atom. The fragmentation of methanethiol is shown in Fig. 1. The following processes take place with an increase in excitation energy:

$$CH_3SH \longrightarrow CH_3SH^+ \tag{1}$$

$$CH_3SH^+ \longrightarrow CH_3S^+ + H \tag{2}$$

$$CH_3S^+ \longrightarrow CHS^+ + H_2 \tag{3}$$

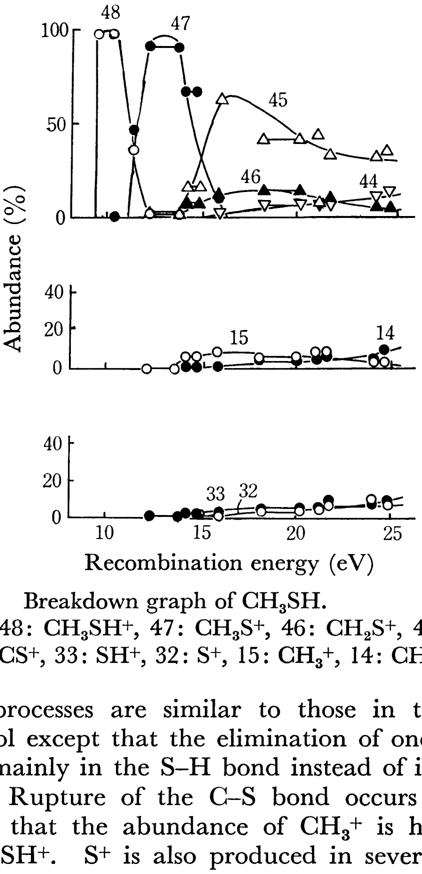


Fig. 1. Breakdown graph of CH_3SH.
m/e 48: CH_3SH^+, 47: CH_3S^+, 46: CH_2S^+, 45: CHS^+, 44: CS^+, 33: SH^+, 32: S^+, 15: CH_3^+, 14: CH_2^+.

These processes are similar to those in the case of methanol except that the elimination of one hydrogen occurs mainly in the S–H bond instead of in the C–H bonds. Rupture of the C–S bond occurs in such a manner that the abundance of CH_3^+ is higher than that of SH^+. S^+ is also produced in several percents in the higher energy region. For the appearance of the S^+ ion, rupture of both the C–S and S–H bonds must occur. It is clear that the S^+ ion is not derived from SH^+, judging from the breakdown curves in Fig.

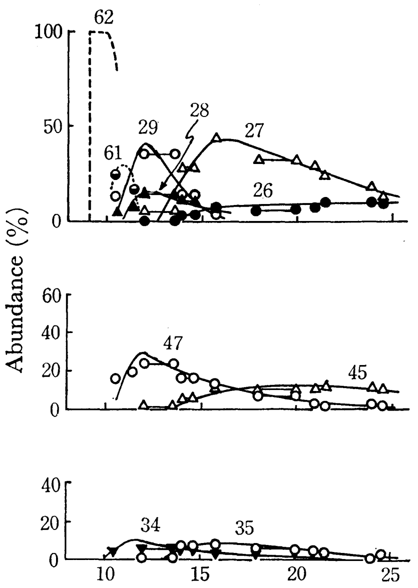


Fig. 2. Breakdown graph of C_2H_5SH.
m/e 62: $C_2H_5SH^+$, 61: $C_2H_5S^+$, 47: CH_2SH^+, 45: CHS^+, 35: SH_3^+, 34: SH_2^+, 29: $C_2H_5^+$, 28: $C_2H_4^+$, 27: $C_2H_3^+$, 26: $C_2H_2^+$.

1. Therefore, the remaining possibility is as follows:

$$CH_3S^+ \longrightarrow CH_3 + S^+ \tag{4}$$

The tendency of the breakdown curves in Fig. 1 supports CH_3S^+ as the major precursor of S^+.

Ethanethiol: The fragmentation of ethanethiol is shown in Fig. 2.

The major processes in the breakdown phenomena of the parent ion are (i) rupture of the C–C bond and (ii) that of the C–S bond.

In the C–C bond rupture the following processes are observed:

$$C_2H_5SH^+ \longrightarrow CH_2SH^+ + CH_3 \tag{5}$$

$$CH_2SH^+ \longrightarrow CHS^+ + H_2 \tag{6}$$

In place of CH_2SH^+ in Reaction 5 the CH_3^+ ion whose abundance is a few percent at maximum is formed by the process:

$$C_2H_5SH^+ \longrightarrow CH_2SH + CH_3^+ \tag{7}$$

In the C–S bond rupture the following processes occur predominantly:

$$C_2H_5SH^+ \longrightarrow C_2H_5^+ + SH \tag{8}$$

$$C_2H_5^+ \longrightarrow C_2H_3^+ + H_2 \tag{9}$$

Besides these processes, hydrogen sulfide elimination from the parent ion occurs as follows:

$$C_2H_5SH^+ \longrightarrow C_2H_4^+ + H_2S \tag{10}$$

The relationship between energy and abundance in Fig. 2 clearly shows that the $C_2H_4^+$ ion is not derived from $C_2H_5^+$.

A small amount of SH_3^+ ion appears in the breakdown graph. This species is probably formed by the process:

$$C_2H_5SH^+ \longrightarrow C_2H_3 + SH_3^+ \tag{11}$$

SH_3^+ has an isoelectronic structure with PH_3 and shows high stability in the mediam energy region (15—20 eV).

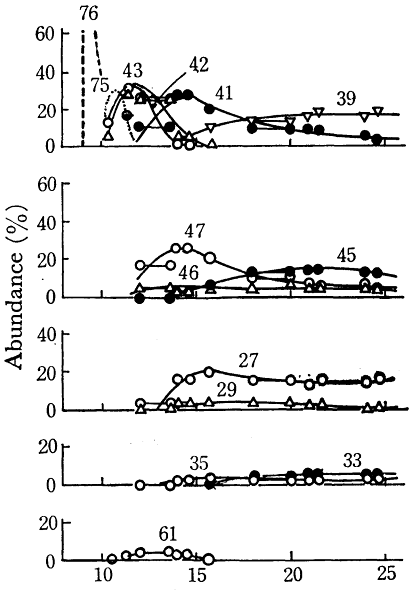


Fig. 3. Breakdown graph of 1-propanethiol.
m/e 76: $C_3H_7SH^+$, 75: $C_3H_7S^+$, 61: $C_2H_4SH^+$, 47: CH_2SH^+, 46: CH_2S^+, 45: CHS^+, 43: $C_3H_7^+$, 42: $C_3H_6^+$, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 35: SH_3^+, 33: SH^+, 29: $C_2H_5^+$, 27: $C_2H_3^+$.

1-Propanethiol: The breakdown graph of 1-propanethiol is shown in Fig. 3. (i) Rupture of the C–S bond and (ii) that of the C–C bonds are observed.

In the C–S bond rupture the following processes occur as energy increases:

$$C_3H_7SH^+ \longrightarrow C_3H_7^+ + SH \tag{12}$$

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \tag{13}$$

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \tag{14}$$

Elimination of hydrogen sulfide occurs in the low energy region in the same manner as Reaction 10.

$$C_3H_7SH^+ \longrightarrow C_3H_6^+ + H_2S \tag{15}$$

The mechanism of formation of the ion $C_2H_3^+$ is not clear, but the following processes are reasonable, judging from the energy relation in the figure:

$$C_3H_6^+ \longrightarrow C_2H_3^+ + CH_3 \tag{16}$$

$$C_3H_7^+ \longrightarrow C_2H_3^+ + CH_4 \tag{17}$$

The formation of SH_3^+ seen in Fig. 3 may be due to the rearrangement of $C_3H_7SH^+$ followed by decomposition:

$$C_3H_7SH^+ \longrightarrow [C_3H_5SH_3^+] \longrightarrow C_3H_5 + SH_3^+ \tag{18}$$

The probability of scission of the $C(\alpha)$–$C(\beta)$ bond is higher than that of the $C(\beta)$–$C(\gamma)$ bond. A similar observation has been made in the case of 1-propanol.[3]

$$C_3H_7SH^+ \longrightarrow CH_2SH^+ + C_2H_5 \tag{19}$$

$$C_3H_7SH^+ \longrightarrow C_2H_4SH^+ + CH_3 \tag{20}$$

As the energy increases CH_2SH^+ decomposes into a hydrogen molecule and CHS^+.

$$CH_2SH^+ \longrightarrow CHS^+ + H_2 \tag{21}$$

2-Propanethiol: The mass spectroscopic patterns obtained by electron impact[13] show distinct differences in the cases of 1-propanethiol and 2-propanethiol. Posi-

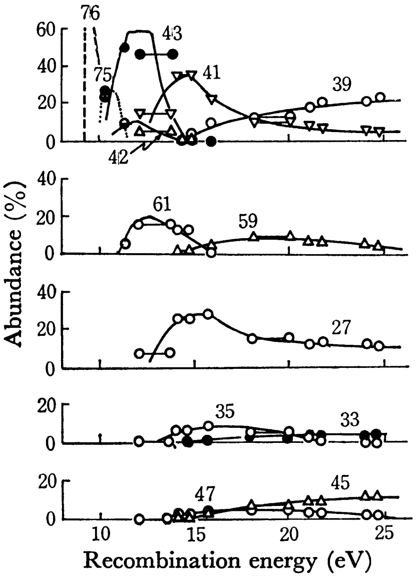


Fig. 4. Breakdown graph of 2-propanethiol.
m/e 76: $C_3H_7SH^+$, 75: $C_3H_7S^+$, 61: $C_2H_4SH^+$, 59: $C_2H_3S^+$, 47: CH_2SH^+, 45: CHS^+, 43: $C_3H_7^+$, 42: $C_3H_6^+$, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 35: SH_3^+, 33: SH^+, 27: $C_2H_3^+$.

tive ion impact using a tandem mass spectrometer is often more useful to understand the fragmentation mechanisms than electron impact is.

The fragmentation of 2-propanethiol is shown in Fig. 4. In the case of the C–S rupture the following process takes place to give $CH_3CHCH_3^+$:

$$i\text{-}C_3H_7SH^+ \longrightarrow CH_3CHCH_3^+ + SH \qquad (22)$$

As energy increases the ion $CH_3CHCH_3^+$ decomposes by the following processes:

$$CH_3CHCH_3^+ \longrightarrow C_2H_3^+ + CH_4 \qquad (23)$$

$$CH_3CHCH_3^+ \longrightarrow C_3H_5^+ + H_2 \qquad (24)$$

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \qquad (25)$$

The rearrangement product SH_3^+ is more abundant in 2-propanethiol (about 10% at maximum) than in 1-propanethiol (4% at maximum). This fact clearly shows that the hydrogen atoms attached to the β carbons are involved in the rearrangement reaction, and it is likely that the probability of the rearrangement depends on the number of the hydrogen atoms available.

In the case of the C–C bond rupture the following reaction occurs:

$$(CH_3)_2CHSH^+ \longrightarrow C_2H_4SH^+ + CH_3 \qquad (26)$$

As the energy increases this $C_2H_4SH^+$ ion seems to decompose by the following processes:

$$C_2H_4SH^+ \longrightarrow C_2H_3^+ + H_2S \qquad (27)$$

$$C_2H_4SH^+ \longrightarrow SH_3^+ + C_2H_2 \qquad (28)$$

*1-Butanethiol (*n*-Butyl Mercaptan)*: The fragmentation of 1-butanethiol is shown in Fig. 5. In the case of the C–S bond rupture the hydrogen sulfide elimination process,

$$C_4H_9SH^+ \longrightarrow C_4H_8^+ + H_2S \qquad (29)$$

occurs as well as the following process,

$$C_4H_9SH^+ \longrightarrow C_4H_9^+ + SH \qquad (30)$$

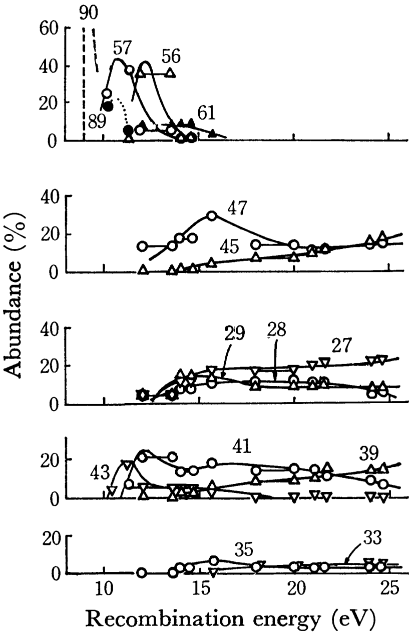


Fig. 5. Breakdown graph of 1-butanethiol.
m/e 90: $C_4H_9SH^+$, 89: $C_4H_9S^+$, 57: $C_4H_9^+$, 56: $C_4H_8^+$, 47: CH_2SH^+, 45: CHS^+, 43: $C_3H_7^+$, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 35: SH_3^+, 33: SH^+, 29: $C_2H_5^+$, 28: $C_2H_4^+$, 27: $C_2H_3^+$.

$C_3H_7^+$ and $C_2H_5^+$ are probably produced by the direct scission of the C–C bonds from the parent ion; the molecular orbital calculation in Table 2 shows the presence of these ions as the primary scission products from the parents.

$$C_4H_9SH^+ \longrightarrow C_3H_7^+ + CH_2SH \qquad (31)$$

$$C_4H_9SH^+ \longrightarrow C_2H_5^+ + C_2H_4SH \qquad (32)$$

An alternative path for the formation of the ion $C_2H_5^+$ is $C_4H_9^+ \rightarrow C_2H_5^+ + C_2H_4$. The energy relationship in Fig. 5 shows that this process is possible. Formation of the $C_3H_3^+$ or $C_2H_3^+$ ions in the median and higher energy region in the figure will be explained by successive elimination of hydrogen molecules or by rupture of the C–C bonds in $C_4H_8^+$ *etc.*

The formation of $C_2H_4SH^+$ and CH_2SH^+ occurs by the following process:

$$C_4H_9SH^+ \longrightarrow C_2H_4SH^+ + C_2H_5 \qquad (33)$$

$$C_4H_9SH^+ \longrightarrow CH_2SH^+ + C_3H_7 \qquad (34)$$

2-Methyl-1-propanethiol (Isobutyl Mercaptan): The breakdown graph of this substance is shown in Fig. 6. The formation of $C_4H_8^+$ and $C_4H_9^+$ by the processes shown in Reactions 29 and 30 appears clearly in the figure. Besides these species, $C_3H_7^+$ in Reaction 31 and its degradation product ions, $C_3H_5^+$ and $C_3H_3^+$, appear also. The ion $C_2H_5^+$ or $C_2H_3^+$ may be a secondary or tertiary product due to a rearrangement of hydrogen atoms on the carbon skeleton. CH_2SH^+ in Reaction 34 is also detectable in this case.

*1-Methyl-1-propanethiol (*sec*-Butyl Mercaptan)*: Figure 7 shows the fragmentation of the substance. In this case formation of $C_4H_8^+$ by hydrogen sulfide elimination from the parent ion is a rather small possibility, and the ion $C_4H_9^+$ appears to be important. It is

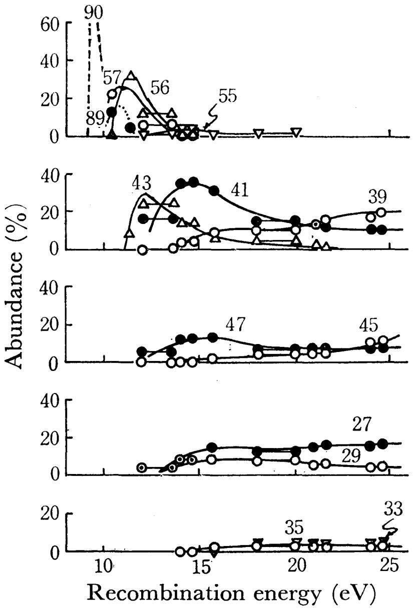


Fig. 6. Breakdown graph of 2-methyl-1-propanethiol. *m/e* 90: $C_4H_9SH^+$, 89: $C_4H_9S^+$, 57: $C_4H_9^+$, 56: $C_4H_8^+$, 55: $C_4H_7^+$, 47: CH_2SH^+, 45: CHS^+, 43: $C_3H_7^+$, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 35: SH_3^+, 33: SH^+, 29: $C_2H_5^+$, 27: $C_2H_3^+$.

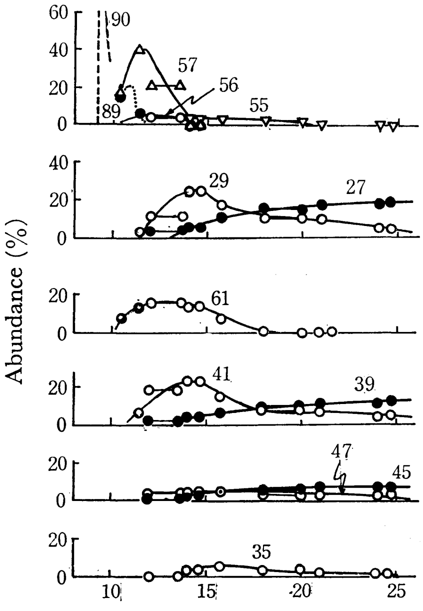


Fig. 7. Breakdown graph of 1-methyl-1-propanethiol. *m/e* 90: $C_4H_9SH^+$, 89: $C_4H_9S^+$, 61: $C_2H_4SH^+$, 57: $C_4H_9^+$, 56: $C_4H_8^+$, 55: $C_4H_7^+$, 47: CH_2SH^+, 45: CHS^+, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 35: SH_3^+, 29: $C_2H_5^+$, 27: $C_2H_3^+$.

interesting to see that $C_2H_4SH^+$ is prominent in the lower energy region (10—15 eV). The ion $C_2H_5^+$ is produced probably by direct scission from the parent ion. $C_3H_5^+$ is produced not as a degradation product from $C_3H_7^+$, but as a product which is derived probably from $C_4H_9^+$ by elimination of CH_4.

$$C_4H_9SH^+ \xrightarrow{-SH} C_4H_9^+ \xrightarrow{-CH_4} C_3H_5^+ \tag{35}$$

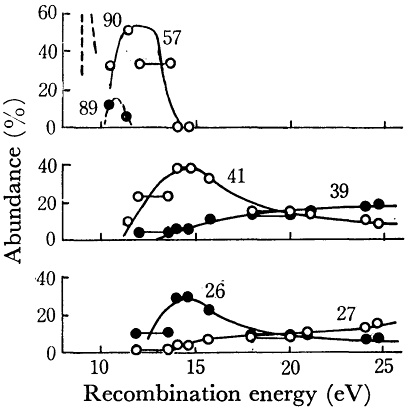


Fig. 8. Breakdown graph of 2-methyl-2-propanethiol. *m/e* 90: $C_4H_9SH^+$, 89: $C_4H_9S^+$, 57: $C_4H_9^+$, 41: $C_3H_5^+$, 39: $C_3H_3^+$, 29: $C_2H_5^+$, 27: $C_2H_3^+$.

*2-Methyl-2-propanethiol (*tert*-Butyl Mercaptan)*: Figure 8 shows the breakdown curves for this substance. The processes which are prominent for this substance involve formation of the $C_4H_9^+$ and $C_3H_5^+$ ions as in Reaction 35. Besides these, the ion $C_2H_5^+$ appears as a fragmentation product from $C_4H_9^+$ after rearrangement of the hydrogen atoms. In this case formation of $C_4H_8^+$ by elimination of hydrogen sulfide is only a slight possibility.

Discussion

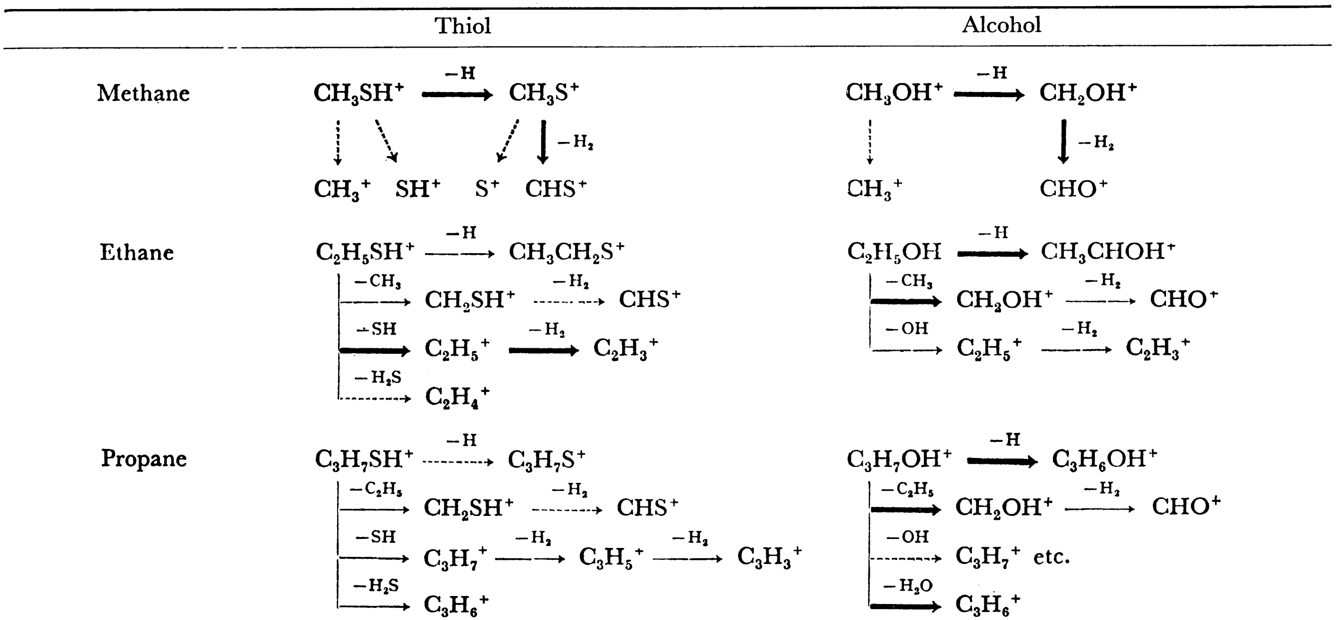
The comparison of the present results of fragmentation in CH_3SH, C_2H_5SH, and 1-C_3H_7SH with those in CH_3OH, C_2H_5OH, and 1-C_3H_7OH obtained by Lindholm and coworkers[1–3] is summarized in Table 1. Only the main processes are listed in the table.

In methanethiol the main processes of hydrogen elimination are similar to those in methanol.[2,5] However, the SH^+ and S^+ ions are observed in methanethiol, whereas almost no OH^+ and O^+ ions are observed in methanol. The presence of SH^+ and the absence of OH^+ reflect the difference of bond strength between C–S and C–O. The bond energy of C–S ($\sim$70 kcal/mol) is larger than that of C–O ($\sim$90 kcal/mol).[14] The major precursor of the S^+ ion is not SH^+ but CH_3S^+, judging from the energy relation in Fig. 1.

In ethanethiol the fragmentation processes are rather different from those in ethanol. Hydrogen elimination is less important in ethanethiol than in ethanol. Elimination of hydrogen sulfide can be observed in ethanethiol, whereas almost no elimination of water is observed in ethanol. Formation of CH_2OH^+ in ethanol is much more important than that of CH_2SH^+ in ethanethiol, probably owing to the difference of stability between them. The rupture of the C–S bond occurs more easily than that of the C–O bond does.

In propanethiol hydrogen elimination from the parent ion is less important than in propanol. Hydrogen sulfide elimination from the parent ion $C_3H_7SH^+$ is prominent, but water elimination from $C_3H_7OH^+$ giving $C_3H_6^+$ is much more prominent than hydrogen sulfide elimination. The rupture of the C–S bond giving $C_3H_7^+$ is easier than that of the C–O bond, owing to the difference of the bond strength between them.

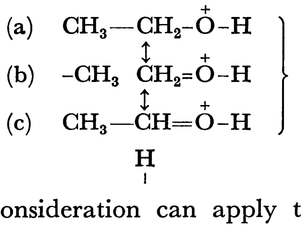
Table 1. Comparison of fragmentation by charge exchange with positive ions between thiols and alcohols



→ important (>40%) → moderately important (40—20%) ⇢ less important (<20%)

Formation of CH_2SH^+ is less prominent than that of CH_2OH^+.

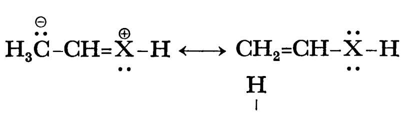
In the case of ethanol, for example, Koch and Lindholm[1)] discussed the suggestion that the ionized oxygen atom has a valency of three and has a tendency towards formation of a double bond between C and O^+. Owing to this tendency, the other bonds of the carbon atom are weakened. They considered the following three resonant structures:



$$\left.\begin{array}{ll}\text{(a)} & CH_3—CH_2\text{-}\overset{+}{O}\text{-}H \\ & \updownarrow \\ \text{(b)} & \text{-}CH_3\ CH_2=\overset{+}{O}\text{-}H \\ & \updownarrow \\ \text{(c)} & CH_3—\underset{H}{CH}=\overset{+}{O}\text{-}H\end{array}\right\} \qquad (36)$$

A similar consideration can apply to the cases of the higher alcohols and also to the cases of the corresponding thiols. Stabilization through an electron-releasing conjugative effect is well known to occur in the following manner:

$$H_2C=\underset{\cdot\cdot}{\overset{+}{X}}\text{-}H \longleftrightarrow H_2\overset{+}{C}\text{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}\text{-}H \qquad (37)$$



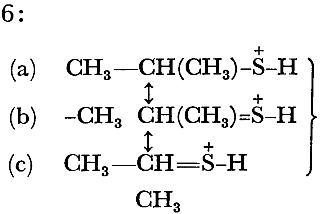
$$H_3\overset{\ominus}{\overset{\cdot\cdot}{C}}\text{-}CH=\underset{\cdot\cdot}{\overset{\oplus}{X}}\text{-}H \longleftrightarrow CH_2=\underset{H}{CH}\text{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}\text{-}H \qquad (38)$$

where X is O or S. As the π-bonding between C2p and S3p is weaker than that between C2p and O2p, rupture of the C–S bond occurs more easily than that of the C–O bond does. This tendency is pronounced in Table 1. The ions CH_2OH^+ and CH_3CHOH^+ (or $CH_3CH_2CHOH^+$) are remarkable compared to the ions $C_2H_5^+$ and $C_3H_7^+$, which are produced by the C–O rupture in the cases of ethanol and 1-propanol. On the other hand, the ions CH_2SH^+ and CH_3CHSH^+ (or $CH_3CH_2CHSH^+$) are not more abundant than $C_2H_5^+$ and $C_3H_7^+$ in the cases of ethanethiol and 1-propanethiol.

Hydrogen sulfide or water elimination from the molecular ions occurs easily in the larger thiols or alcohols. This process seems to proceed through the intermediate $R–SH_2^+$ or $R–OH_2^+$, which probably weakens the double bond formation between R–S or R–O in Reaction 36 (a) and (b) and therefore results in the rupture of the bond R–S or R–O in the lower energy region.

For the compounds larger than *n*-propyl, the apparent similarity is more pronounced for thiols and alcohols.[7)] Increase of the length of the carbon chain causes a larger contribution of the alkyl group which is common to thiols and alcohols. This makes the fragmentation pattern similar for larger thiols and alcohols. However, the larger cross section of the sulfur atom in thiols for charge exchange or electron impact compared with that of oxygen in alcohols makes the parent ion more prominent in thiols. This fact will be confirmed by the study using a double mass spectrometer cross section measurement.[15)]

Next, let us consider the effect of the structure of the compound. Methyl elimination from 2-propanethiol (SH: secondary position) giving C_2H_4SH is remarkable, whereas that from 1-propanethiol has only a small probability. For 2-propanethiol the following resonance forms should be considered in the same manner as Reaction 36:



$$\left.\begin{array}{ll}\text{(a)} & CH_3—CH(CH_3)\text{-}\overset{+}{S}\text{-}H \\ & \updownarrow \\ \text{(b)} & \text{-}CH_3\ CH(CH_3)=\overset{+}{S}\text{-}H \\ & \updownarrow \\ \text{(c)} & CH_3—\underset{CH_3}{CH}=\overset{+}{S}\text{-}H\end{array}\right\} \qquad (39)$$

As (b) and (c) are the same expression, only the resonance between (a) and (b) can be taken in account here. Thus it is easily understood why methyl elimination from the molecular ion is highly probable in 2-propanethiol. On the other hand, it is obvious that 1-propanethiol loses its methyl group by a different mechanism. The ionic species $CH_2{=}\overset{+}{S}{-}H$ is known to be more abundantly produced than $CH_3CH{=}\overset{+}{S}{-}H$ on electron impact of 1-propanethiol. Generally the β-cleavage is easier than the γ-cleavage for sulfur-containing ions.[16] The same tendency is more pronounced for the case of electron impact mass patterns in 1- and 2-propanols.[17]

The difference of the mass patterns between 1-(primary) and 2-(secondary) butanethiols can be understood in principle in the same manner as stated above. The prominent ions CH_2SH^+ in 1-butanethiol and $C_2H_4SH^+$ in 2-butanethiol and formed through the resonance containing the C=S double bond.

Fragmentation of the tertiary compound of butyl mercaptan is entirely different from the other butyl mercaptan. It is initiated by rupture of the labile C–S bond. Not only hydrogen migration but also rearrangement of the carbon structure are involved in the decomposition processes.

In previous papers,[18–20] we have studied the possibility of direct fragmentation of the molecular ions from their electronically excited states. We found that this is true for various systems, by comparing the experimental results with those obtained by calculation. As calculation of methanethiol has been done in the other paper[21] submitted in this bulletin, only the results of the calculation for two kinds of propanethiols and four kinds of butanethiols are shown here. According to the Extended Hückel Molecular Orbital (EHMO) method the energy levels and eigenvectors of the molecular orbitals are calculated, and the main characters of the MO's are determined on the basis of these calculated eigenvectors. When an electron is ejected from a certain molecular orbital by charge exchange, the bond corresponding to the molecular orbital is subjected to scission, resulting in formation of various fragment ions. The energy levels, the main characters, and the product ions expected are shown in Tables 2 and 3 for propanethiols and for butanethiols, respectively. The tendency of appearance of the ions is in good agreement with the experimental results in Figs. 3 and 4 for propanethiols, and the same is true

TABLE 2. CALCULATED MO ENERGY, CALCULATED MO ASSIGNMENT, AND FRAGMENT IONS FOR 1-PROPANETHIOL AND 2-PROPANETHIOL

	Calculated MO energy (eV)	Main character	Produced ions
1-Propanethiol	10.39	n(S)	76
	11.53	n(S) σ(SH)	76, 75
	13.03	$\sigma(C_1S)$ $\sigma(C_1C_2)$ $\sigma(C_2C_3)$	43, 42, 47 or 29, 61
	13.29	$\pi(CH_2)$	
	13.55	$\sigma(C_1C_2)$	47 or 29
2-Propanethiol	10.38	n(S)	76
	11.45	n(S) σ(SH)	76, 75
	13.13	$\sigma(C_2S)$	43 or 42
	13.26	$\sigma(C_1C_2)$ $\sigma(C_2C_3)$	61

TABLE 3. CALCULATED MO ENERGY, CALCULATED MO ASSIGNMENT, AND FRAGMENT IONS FOR VARIOUS BUTANETHIOLS

	Calculated MO energy (eV)	Main character	Produced ions
1-Butanethiol	10.40	n(S)	90
	11.52	σ(SH) $\sigma(C_1S)$	89, 57 or 56
	12.75	$\sigma(C_1S)$ $\sigma(C_2C_3)$	57 or 56, 61 or 29
	13.24	$\pi(CH_2)$	
	13.47	$\sigma(C_1C_2)$	47 or 43
2-Methyl-1-propanethiol	10.36	n(S)	90
	11.44	σ(SH) $\sigma(C_1S)$	89, 57 or 56
	12.95	$\sigma(C_1C_2)$	43 or 47
	13.10	$\sigma(C_2C_m)$	
1-Methyl-1-propanethiol	10.37	n(S)	90
	11.35	n(S) σ(SH) $\sigma(C_1S)$	89, 57 or 56
	12.87	$\sigma(C_1C_2)$ $\pi(CH_2)$	61 or 29
	13.09	$\sigma(C_1S)$ $\pi(CH_2)$	57 or 56
2-Methyl-2-propanethiol	10.36	n(S)	90
	11.45	n(S) σ(SH)	90, 89
	13.01	$\sigma(C_2S)$	57

C_m: C in 2-methyl group.

for butanethiols (see Figs. 5—8). It is likely that there is direct scission, which will give the various fragment ions shown in Tables 2 and 3. Even if all of the fragment ions are not derived from the direct scission of the molecular ions, at least some parts of these ions are considered to be formed by the scission from the electronically excited molecular ions. As the fragmentation processes in the higher energy region are profoundly influenced by the secondary scission, it is obvious that the calculation performed above cannot apply to the processes in the higher energy region.

From Table 2, it is shown that fragmentation in 2-propanethiol is simpler than that in 1-propanethiol; this tendency is in agreement with that obtained in the experimental results (Figs. 3 and 4). Similarly, from Table 3 fragmentation of 2-methyl-2-propanethiol (tertiary compound) is expected to be simpler than that of any other compounds of butanethiol. This tendency is in agreement with that obtained by the experiments in Figs. 5—8.

It is noteworthy that this kind of study using a double mass spectrometer can supply information about ion-molecule reactions involving the excited parent ions; it is especially useful to obtain the energy-abundance relation among the fragment ions.

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