Structure and Fragmentations of $[C_3H_7S]^+$ Ions†

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The principal fragmentation reactions of metastable $[C_3H_7S]^+$ ions are loss of H_2S and C_2H_4. These reactions and the preceding isomerizations of $[C_3H_7S]^+$ ions with six different initial structures were studied by means of labelling with ^{13}C or D. From the results it is concluded that the loss of H_2S and C_2H_4 both occur at least mainly from ions with the structure $[CH_3CH_2CH{=}SH]^+$ or from ions with the same carbon sulfur skeleton, with the exception of the ions with the initial structure $[CH_3CH_2S{=}CH_2]^+$, which partly lose C_2H_4 without a preceding isomerization. For all ions, more than one reaction route leads to $[CH_3CH_2CH{=}SH]^+$. It is concluded that the loss of H_2S is at least mainly a 1,3-elimination from the $[CH_3CH_2CH{=}SH]^+$ ions. Both decomposition reactions are preceded by extensive but incomplete hydrogen exchange.

INTRODUCTION

Recently it was shown that $[C_3H_7S]^+$ ions, generated with different structures, lose ethylene and hydrogen sulfide with almost identical metastable intensity ratios. This suggests isomerization to a common structure and decomposition through the same reaction channels.[1] Labelling with ^{13}C and D of ions with initial structure *a* gave a firm indication that these ions rearrange via a cyclic intermediate *f* before loss of ethylene occurs. The fragmentation was thought[1] to occur from structure *c*, as shown in Scheme 1. The ions with initial structure *b* are a possible exception since not only did they show a somewhat different metastable intensity ratio, but the D labelling suggested some direct fragmentation, according to Scheme 2.[1]

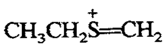
A completely different behaviour pattern was observed for $[C_3H_7S]^+$ ions with lower internal energy.[2,3] Seven types of ions (*a*–*g*) had lifetimes $\geqslant 10^{-5}$ s and were identifiable from their collisional activation (CA) spectra. Ions formed as *h* rearrange within that time to a mixture of *d* and *a* and ions with initial structure *i* rearrange to *c*. For ions *e* and *f* partial isomerization was observed to *a* and *c* respectively.[2,3] Ions of type *e* have been shown to be stable in the ICR cell,[4] but metastable ions with lifetimes of 10^{-6}–10^{-5} s of the same structure all undergo a ring opening reaction to *a*.[3] This is probably one of the best examples of the dependence of the degree of isomerization on internal energy.

As has been emphasized before,[1,3] this situation is very different from that of the analogous $[C_3H_7O]^+$ and $[C_3H_8N]^+$ ions. Four types of acyclic $[C_3H_7O]^+$ ions show different metastable ion characteristics[5] and CA spectra.[6] Cyclic $[C_3H_7O]^+$ ions *j*, for which a heat of formation of 169 kcal mol^{-1} was estimated,[4] could not be detected from the CA spectra.[3,6] Recently, a detailed description of the potential energy surfaces for rearrangements between some $[C_3H_7O]^+$ ions was given.[7] It was shown that the ions *k* ($\Delta H_f = 158$ kcal mol^{-1}) are readily formed from $[CH_3CHCH_2OH]^+$ ($\Delta H_f = 161$ kcal mol^{-1}), a plausible intermediate in the decomposition pathway of $[CH_3CH_2CH{=}OH]^+$ ions ($\Delta H_f = 134$ kcal mol^{-1}) to C_2H_4 and $[CH_3O]^+$.

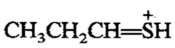
The cyclic ions *e* and *f* are probably quite stable as compared with the non-cyclic isomers. For $[C_2H_5S]^+$ ions it was found that the cyclic isomer is the most


$CH_3CH{=}\overset{+}{S}CH_3$

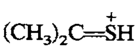
a


$CH_3CH_2\overset{+}{S}{=}CH_2$

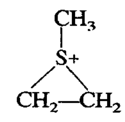
b

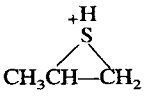

$CH_3CH_2CH{=}\overset{+}{S}H$

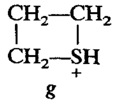
c

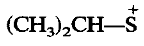

$(CH_3)_2C{=}\overset{+}{S}H$

d


e


f

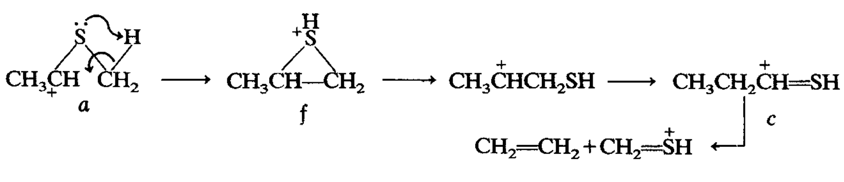

g


$(CH_3)_2CH{-}\overset{+}{S}$

h

$CH_3CH_2CH_2S^+$

i


Scheme 1

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† Part II: for Part I, see Ref. 1.

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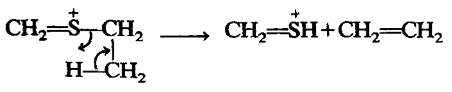
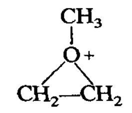
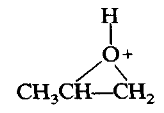


b

Scheme 2



j



k

stable form,[8] a situation very different from that of the oxygen analogues.[9] This has been attributed to a less effective resonance stabilization in the linear $[C_2H_5S]^+$ ions and to less ring strain energy in $[CH_2CH_2SH]^+$ as compared with the oxygen-containing ions.[10] The same arguments will hold for $[C_3H_7S]^+$, but it may be expected that the cyclic ion *f* will have a somewhat higher ΔH_f value relative to the non-cyclic isomers, since it is not stabilized as effectively by the extra methyl group as *a* to *d*. Nevertheless, its formation in (rearrangements of $[C_3H_7S]^+$ ions, as has been proposed before,[1] may well be expected.

In this paper the results of a study of isomerization and fragmentation reactions of metastable $[C_3H_7S]^+$ ions by means of labelling with ^{13}C and D are reported. Some investigations on ions with structure *a*, labelled with ^{13}C and D, and on an ion *b*, labelled with D, have been described before.[1]

RESULTS AND DISCUSSION

Formation of ions

Ions with structure *b*, labelled with deuterium, were obtained from the molecular ions of labelled diethyl sulfides and $[CH_3CH_2S{=}^{13}CH_2]^+$ (b_1) was generated from $[(CH_3CH_2S^{13}CH_2)_2]^{+\cdot}$. Both reactions are normal α-cleavages. In the same way ions *c*, labelled with ^{13}C or D and ions *d*, labelled with D, were obtained from the corresponding pentane-3-thiols and 2-methyl-2-propane thiols respectively.

The $[(CH_3)_2{}^{13}C{=}SH]^+$ ions (d_1) were generated from $[(CH_3)_2{}^{13}CHSH]^{+\cdot}$. These molecular ions may lose hydrogen atoms from three different positions. Labelling with deuterium and calculation along the lines indicated by Meyer and Harrison[11] shows that about 73% of these hydrogens originate from the α position, 7% from the -SH and 20% from the CH_3 groups, but this does not prove that ions *d*, *h* and *f* respectively are formed in this ratio, as H/D exchange may occur in the parent ion. However, when ions *h* are formed, they will rearrange mainly to *d* and ions *f* will rearrange to c.[2] The latter will not disturb our measurements on ions *d* (*vide infra*).

Ions with structure $[CH_2CH_2S^{13}CH_3]^+$ (e_1) are formed from the molecular ions of $(^{13}CH_3SCH_2)_2$ upon loss of a thiomethoxy radical, as may be expected on the grounds of results for analogous compounds.[3] Cyclic ions with structure $[CH_3CH^{13}CH_2SH]^+$ (f_1) are formed from $[CH_3CH(SH)^{13}CH_2CH_2CH_3]^{+\cdot}$ upon loss of an ethyl radical.

Table 1. $[M-CH_3]/[M-CD_3]$ ratios observed and calculated for some deuterated 2-methyl-2-propane thiols and -alcohols

	X=SH			X=OH		
Compound	Source	1st FFR	Calc.	Source	1st FFR	Calc.
$(CD_3)_2C$—X CH_3	0.7	0.8	0.54	0.55	—[a]	0.54
$(CH_3)_2C$—X CD_3	2.7	2.8	2.15	2.2	—[a]	2.14

[a] No metastable transitions could be detected.

For the formation of the ions d_2 and d_3 from deuterium labelled 2-methyl-2-propane thiols an interesting isotope effect was observed. As can be seen from Table 1, the $[M-CH_3]/[M-CD_3]$ ratios measured in the normal 70 eV mass spectra and for decomposition in the 1st field free region (FFR) do not obey normal statistics, but show enhanced loss of a CH_3 radical over a CD_3 radical. A similar effect has been found by Neeter and Nibbering for the loss of a methyl radical from *t*-butylpyridines and *t*-butylbenzenes in the 1st and 2nd FFR.[12] The observed effect must be a secondary isotope effect; it can hardly be understood that upon loss of a methyl radical a C—H(D) bond is broken in one of the other $CH_3(D_3)$ groups. Moreover, in that case it would be expected that loss of a CD_3 would be preferred over CH_3 loss. According to the quasi-equilibrium theory, the rates of reactions for ions of high internal energy are determined by their frequency factors.[13] In that case the ratio of the frequency factors for loss of $CH_3^\cdot$ and $CD_3^\cdot$ can be estimated from the square root of the ratio of the reduced masses of the separating particles.[12] This gives the calculated values of Table 1. For the alcohols the agreement between calculated and observed values is good, for the thiols the observed effects are much greater than calculated in this way. Since sulfides and thiols have relatively low ionization potentials, the ions produced upon α-cleavage are less stable as compared with the oxygen compounds.[15] Therefore, the α-cleavage reactions for sulfides and thiols have relatively large activation energies. This could explain the larger isotope effects for the sulfur compounds as compared with their oxygen analogues. An exact explanation has to be found in the Rice-Ramsperger-Kassel-Marcus theory of unimolecular reactions, but a quantitative treatment is not yet possible.[12,14]

Kinetic energy release

The data for release of kinetic energy upon decomposition of ions *a*, *b*, *c* and *d* are listed in Table 2. All metastable peaks are symmetrical, Gaussian shaped and do not show any composite nature, as far as can be detected without using mathematical methods. Loss of C_2H_4 from ions *a* and *b* is accompanied by a somewhat larger release of kinetic energy than loss of C_2H_4 from *c* and *d*. For loss of H_2S even more pronounced differences are observed. From metastable intensity ratios[1] and the present labelling studies it

Table 2. Measured energy releases in metastable transitions of $[C_3H_7S]^+$ ions[a,b,c]

Ion	Loss of C_2H_4	Loss of H_2S
a $CH_3CH{=}\overset{+}{S}CH_3$	17	22
b $CH_3CH_2\overset{+}{S}{=}CH_2$	17	21
c $CH_3CH_2CH{=}\overset{+}{S}H$	13	5
d $(CH_3)_2C{=}\overset{+}{S}H$	12	12

[a] $T_{50\%}$ in meV.
[b] Corrected for the energy spread of the main beam of stable ions.
[c] Measured on a Vacuum Generators ZAB-2F.

can be concluded that these ions all decompose, at least for the main part, through the same reaction channels. The dissimilarities in the release of kinetic energy may be caused by differences in the internal energy of the decomposing ions, but some deviations in the fragmentation mechanism, especially for loss of H_2S (*vide infra*), cannot be excluded for a part of some types of ions.

Loss of ethylene: ^{13}C labelling experiments

Loss of ethylene is one of the major fragmentation reactions of metastable $[C_3H_7S]^+$ ions, independent of their initial structure (Scheme 3). In order to obtain

$$[C_3H_7S]^+ \longrightarrow [CH_3S]^+ + C_2H_4$$

Scheme 3

information about the mechanism of this reaction and the preceding isomerizations, the ions b_1 to f_1, labelled with ^{13}C, were generated. The relative amounts of C_2H_4 and $^{13}CCH_4$, measured for decomposition in the 1st FFR, are given in Table 3. This shows that none of the ions, with the possible exception of ion a_1, decompose by one unique reaction route. Only more complicated reaction schemes can explain the observed values.

First, a striking difference is observed between the two thiols c_1 and d_1: for c_1 only 7% of the α-carbon atoms are found in C_2H_4, for d_1 this is 89%. This can be rationalized by isomerization reactions shown in Scheme 4, leading to decomposing ions with the ^{13}C label in different positions. The ions c_1 almost all (93%) fragment directly to the products p_1, possibly after a 1,3-hydrogen shift to l_1; 7% of the ions rearrange along one or both of the indicated routes to c_2 and decompose to the products p_2. For ions d_1 a logical first step is a 1,2-hydrogen shift to m_1. After that, most ions must rearrange to f_2 and this leads via n_2 and c_2 to p_2. A smaller fraction will react via a 1,2 methyl shift to c_1, and this gives mainly the products p_1.

Table 3. Loss of C_2H_4 and $^{13}CCH_4$ from $[^{13}CC_2H_7S]^+$ ions[a,b]

Ion	C_2H_4	$^{13}CCH_4$
a_1 $CH_3{}^{13}CH{=}\overset{+}{S}CH_3$[c]	0	100
b_1 $CH_3CH_2\overset{+}{S}{=}{}^{13}CH_2$	94	6
c_1 $CH_3CH_2{}^{13}CH{=}\overset{+}{S}H$	93	7
d_1 $(CH_3)_2{}^{13}C{=}\overset{+}{S}H$	11	89
e_1 $\underbrace{CH_2CH_2\overset{+}{S}}{}^{13}CH_3$	89	11
f_1 $CH_3\underbrace{CH^{13}CH_2\overset{+}{S}}H$	90	10

[a] Normalized to a total of 100% for each ion.
[b] Estimated accuracy for b_1-f_1: ±1%, for a_1: ±10%.
[c] Ref. 1.

The D labelling results were rationalized in earlier work[1] by assuming that ions of type *a* rearrange to the cyclic ions *f* (Scheme 1). Ions a_1 will then give f_2 and it may be expected that these intermediates mainly decompose to the products p_2, as has been observed. Scheme 4 suggests that at least a small part of the ions f_2 would rearrange via m_1 to c_1, and give rise to formation of C_2H_4. This has not been found, but the method used was not accurate enough to exclude formation of less than 10% C_2H_4.

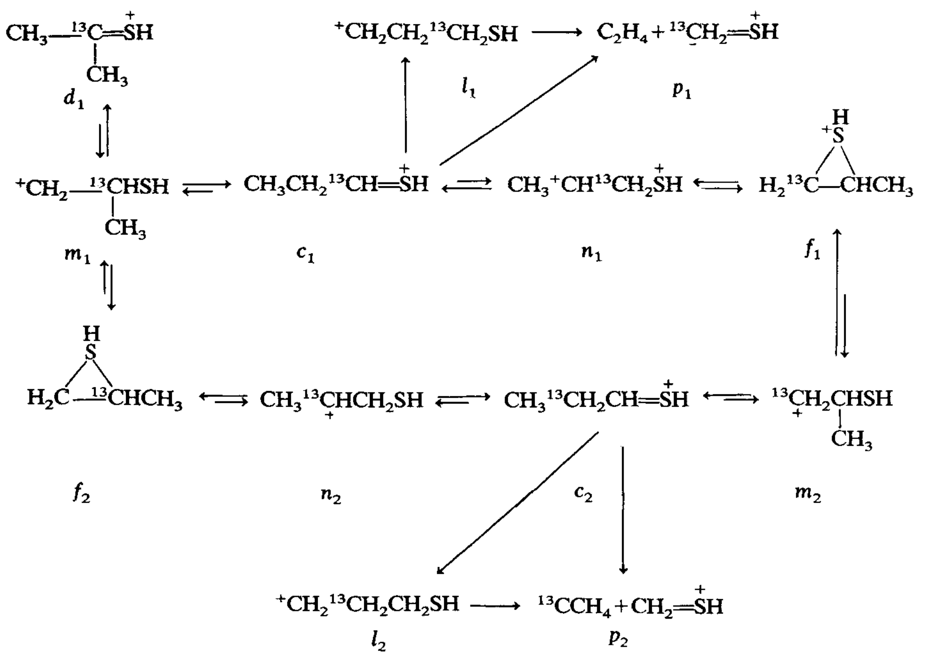
The results for the ions b_1 can be explained in the following way. One might expect that ions b_1 rearrange to f_1 along one or both of the routes given in Scheme 5. Further isomerization and decomposition as given in Scheme 4 would give products p_1 and p_2. In good agreement with this, ions generated directly with structure f_1 show 90% loss of C_2H_4 and 10% loss of $^{13}CCH_4$. This result is completely compatible with that for ions d_1. The excess of C_2H_4 over $^{13}CCH_4$ for ions b_1 is most probably caused by a direct fragmentation of ions b_1 according to Scheme 2. Firm support for this is obtained by the results of D labelling, from which it is estimated that only about 45% of the ions *b* decompose after a rearrangement via *f*. Metastable ion intensity ratios do at least not exclude the existence of a different fragmentation route for ions *b* as compared with other ions.

Ions with structure *e* may be expected to isomerize to *a* and strong evidence for this has indeed been obtained.[2] If so, e_1 will give a_2 and this ion will rearrange to f_1 (Scheme 5). According to Scheme 4, this will lead to loss of both C_2H_4 and $^{13}CCH_4$. These results are again completely compatible with those for ions d_1, as discussed above. If ions e_1 all decompose via f_1, the formation of about 10% $^{13}CCH_4$ and 90% C_2H_4 would be expected. This is in good agreement with the observed values (Table 3) and therefore supports the proposed fragmentation scheme.

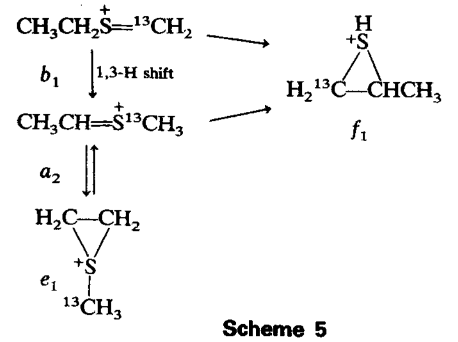
The observed ratios of C_2H_4 and $^{13}CCH_4$ can all be understood remarkably well in this way. It should be kept in mind that ions formed from different precursors can have different internal energies and the energy range giving rise to metastable transitions is broad (>1 eV for reactions with low frequency factors). Therefore, these differences in the internal energy of the intermediates could have led to greater discrepancies in the product ratios than actually observed.

Loss of ethylene: D labelling experiments

Results for loss of ethylene from several D labelled ions with structure *a* and from one ion with structure *b* have been given earlier.[1] Extensive H/D exchange precedes the fragmentation, leading to mixtures of



Scheme 4



Scheme 5

products with different H/D content. For ions *a* the product ratio could be explained by isomerization of *a* via *f* to *c*, accompanied by complete scrambling of all H and D atoms, except one H/D of the methyl group. In the following section results are given for ions of types *b*, *c* and *d*. The estimated accuracy for all observed values is ±2.

$[CH_3CH_2S{=}CH_2]^+$ (b). The observed relative intensities of the metastable transitions for loss of $C_2H_xD_{4-x}$ from ions with structure *b* in the 1st FFR are given in Table 4, together with intensities calculated for three different reaction pathways (A, B and C). Although it is clear that H/D exchange occurs in all ions, loss of C_2D_4 from b_2 could not be detected and has to be <0.2%, although b_2 contains four deuterium atoms. This indicates a rearrangement to an ion in which one of these atoms occupies a position in which it is not involved in the H/D exchange process and in the elimination of ethylene. Unexpectedly, ions b_3 and b_4 both lose some C_2H_4, so these ions do not provide information about which of the α-D atoms of b_2 moves to this special position. The results are best explained by an isomerization of part of the ions *b* to ions *a* and subsequent rearrangement to *f*, according to Scheme 5. One of the α-H/D atoms of the ethyl group of *b* moves to the methylene group and of the newly formed methyl group either an H or a D migrates to the sulfur atom upon formation of *f*. The latter H/D may therefore originate from both α positions of *b*. Ions *f* will rearrange to a *n*-propylene thiol structure (*c*, *l* or *n*) and decompose as given in Scheme 4. However, this reaction pathway cannot be followed by all ions, as the fraction of C_2H_3D from b_3 and b_4 would then have been much greater than observed. For the *n*-propylene thiol ions extensive H/D exchange has to be expected, as this was also observed for ions with initial structure *c* (*vide infra*). Therefore, the results indicate a contribution of a fragmentation directly from structure *b* (Scheme 2), without preceding H/D exchange reactions. The possibility, that ions *b* rearrange directly to *f* (Scheme 5) has also to be considered. The label distribution in the fragmenting ions will then be different for b_3, b_4 and b_5. When it is assumed that in the *n*-propylene thiol ions the six H/D atoms of the propylene group are completely scrambled before fragmentation, it can be calculated from the ratio of C_2H_3D, $C_2H_2D_2$ and C_2HD_3 observed for

Table 4. Intensities[a] of the metastable transitions for loss of $C_2H_xD_{4-x}$ from D labelled ions with structure *b*

Ion	Fragment lost	Observed	Calculated[b] A	B	C
b_2 $CH_3CD_2\overset{+}{S}{=}CD_2$	C_2H_3D	11	9	9	9
	$C_2H_2D_2$	81	82	82	82
	C_2HD_3	8	9	9	9
b_3 $CH_3CD_2\overset{+}{S}{=}CH_2$	C_2H_4	7	15	7	9
	C_2H_3D	28	30	26	27
	$C_2H_2D_2$	65	55	67	65
b_4 $CH_3CH_2\overset{+}{S}{=}CD_2$	C_2H_4	68	58	66	65
	C_2H_3D	24	24	28	27
	$C_2H_2D_2$	8	18	6	8
b_5 $CD_3CD_2\overset{+}{S}{=}CH_2$	$C_2H_2D_2$	10	18	6	8
	C_2HD_3	27	24	28	27
	C_2D_4	63	58	66	65

[a] The intensities are normalized to a total of 100% for each ion.
[b] For the method of calculation of the expected intensities for pathways A, B and C, see text.

b_2, that 55% of the ions *b* eliminate ethylene directly and 45% rearrange via *f* before fragmentation.

The product ratios observed for the ions b_4 and b_5 are complementary to a good approximation. This indicates that no isotope effect influences the fragmentation rate. In the calculations of the expected product intensities, which lead to satisfactory agreement with the observed values, no isotope effect was taken into account. Table 4, column A, gives the calculated intensities for the case where the ions *b* rearrange to *f* directly; column B gives the intensities calculated for rearrangement of *b* to *f* via *a*. It is evident that the values obtained by model B are in better agreement with the observed values than those calculated according to model A. The best fit is obtained when it is assumed, that of the ions *b* rearranging to *f*, about 80% follow the route via *a* and 20% isomerize in a one-step process to *f* (column C).

$[CH_3CH_2CH{=}SH]^+$ (*c*) and $[(CH_3)_2C{=}SH]^+$ (*d*). The observed relative intensities for loss of $C_2H_xD_{4-x}$ from ions with structures *c* and *d* are given in Table 5, together with expected intensities calculated for two different modes of H/D exchange prior to decomposition according to Scheme 4 (models A and B). It is evident that hydrogen atoms of the -SH(D) groups are found to some extent in the ejected ethylene molecules. When a random H/D distribution in the alkyl groups is assumed in a first approximation, it can be calculated from the results for ions c_4 and c_7 that about 6% of the thiol hydrogens of ions *c* have exchanged with H/D atoms of the alkyl groups. In the same way it is calculated from the values for ion d_2 that 10.5% of the ions *d* have exchanged the thiol hydrogen atom with alkyl H/D atoms.

As approximately complementary labelled ethylene molecules are expelled from the ions c_4 and c_6, most probably no isotope effect is operative. In Table 5, model A, the calculated intensities are given for a statistical H/D distribution in the alkyl groups and a fragmentation mechanism, in which one of the γ-hydrogen atoms is transferred to the $-CH{=}\overset{+}{S}H$ fragment from which the $[CH_3S]^+$ ion is formed. For most ions, a reasonable agreement with the observed values is obtained, but not for c_5 and d_3. These ions, both containing three deuterium atoms in the alkyl group, show identical label distribution for the ejected ethylene molecules. This indicates that from both ions the same mixture of decomposing ions is formed. In both cases more $C_2H_2D_2$ is observed than calculated by model A.

Table 5. Intensities[a] of the metastable transitions for loss of $C_2H_xD_{4-x}$ from D labelled ions with structures *c* and *d*

Ion	Fragment lost	Observed	Calculated[c] A	Calculated[c] B
c_3 $CH_3CD_2CH{=}\overset{+}{S}H$	C_2H_4	4	7	4
	C_2H_3D	57	54	59
	$C_2H_2D_2$	39	39	37
c_4 $CD_3CD_2CH{=}\overset{+}{S}H$	$C_2H_2D_2$	2	2	2
	C_2HD_3	65	66	64
	C_2D_4	33	32	34
c_5 $CD_3CH_2CH{=}\overset{+}{S}H$	C_2H_3D	12	21	11
	$C_2H_2D_2$	76	60	77
	C_2HD_3	12	19	12
c_6 $CH_3CH_2CD{=}\overset{+}{S}H$	C_2H_4	34	34	33
	C_2H_3D	66	66	67
c_7 $CH_3CH_2CH{=}\overset{+}{S}D$	C_2H_4	96	96	96
	C_2H_3D	4	4	4
d_2 $(CD_3)_2C{=}\overset{+}{S}H$	C_2HD_3	7	7	7
	C_2D_4	93	93	93
d_3 $CD_3(CH_3)C{=}\overset{+}{S}H$[b]	C_2H_3D	12	22	12
	$C_2H_2D_2$	76	59	78
	C_2HD_3	12	19	10

[a] The intensities are normalized to 100% for each ion.

[b] Identical results were obtained for ions d_3 generated from $CD_3(CH_3)_2CSH$ and $CH_3(CD_3)_2CSH$.

[c] For the method of calculation of the expected intensities for pathways A and B, see text.

From the ^{13}C labelling experiments it was concluded, that ions *c* and *d* may rearrange via the cyclic ions *f* before loss of ethylene occurs. When the reaction of *c* to *f*, as given in Scheme 4, is fast and reversible, the α- and β-hydrogen atoms of ions *c* will become completely equivalent. H/D exchange between the γ-position and the α- and β-positions of ions *c* will occur to some extent. In Table 5, model B, the calculated values are given for the case that 6% of the hydrogen atoms of the thiol group are exchanged for H/D atoms of the alkyl groups, the α- and β-positions have become equivalent and statistically 23.3% of the γ-H/D atoms have interchanged their positions with α- and β-H/D atoms. This gives the best fit obtainable by this model and the agreement with the observed values is satisfactory. Although the amount of H/D exchange between the thiol and alkyl group is calculated for the case of complete H/D scrambling in the alkyl group and the degree of H/D exchange actually is less, this does not noticeably influence the results.

For the ions *d* it was concluded from the ^{13}C labelling experiments that a rearrangement to the ions *c*, partially via the cyclic ions *f*, occurs before fragmentation. The degree of H/D exchange in the ions so formed is not necessarily the same as in the directly formed ions *c*, as their internal energy may be different. Nevertheless, a good agreement with the observed intensities is obtained, when the same parameters for H/D exchange in the alkyl group are used as for directly formed ions *c* (Table 5, model B).

Loss of H_2S: D labelling experiments

Besides loss of ethylene, the expulsion of a molecule of hydrogen sulfide is the major reaction of $[C_3H_7S]^+$ ions (Scheme 6). It is evident that a rearrangement of the sulfide-type ions *a* and *b* has to occur before this fragmentation can take place. Information about the reaction can be obtained by labelling with deuterium. D labelled ions with structure *a*, *b*, *c* and *d* have been generated therefore and their fragmentations in the 1st FFR were studied. It appears that loss of H_2S is preceded by extensive hydrogen exchange. For each

$$[C_3H_7S]^+ \longrightarrow [C_3H_5]^+ + H_2S$$

Scheme 6

Table 6. Intensities[a] of the metastable transitions for loss of $H_xD_{2-x}S$ from D labelled ions with structure *c*

Ion	Observed			Calculated[b]		
	H_2S	HDS	D_2S	H_2S	HDS	D_2S
c_3 $CH_3CD_2CH{=}\overset{+}{S}H$	86	14	0	86	14	0
c_4 $CD_3CD_2CH{=}\overset{+}{S}H$	22	74	4	22	74	4
c_5 $CD_3CH_2CH{=}\overset{+}{S}H$	53	46	1	53	46	1
c_6 $CH_3CH_2CD{=}\overset{+}{S}H$	93	7	0	93	7	0
c_7 $CH_3CH_2CH{=}\overset{+}{S}D$	9	91	0	9	91	0

[a] The intensities are normalized to a total of 100% for each ion.
[b] For the method of calculation of the expected intensities, see text.

type of ion it was determined from which positions the hydrogen atoms of the H_2S molecule originate.

$[CH_3CH_2CH{=}SH]^+$ (c). The ratio of H_2S, HDS and D_2S lost from the labelled ions c_3–c_7 is given in Table 6. Loss of D_2S can hardly be detected from ions c_3 (0.2%) and c_5, and although some D_2S is lost from c_4 and some H_2S from c_7, this indicates that the thiol H/D atom is retained to a large extent in the $H_xD_{2-x}S$ molecule. The results also show that the other H/D atom of $H_xD_{2-x}S$ can originate from all other positions.

Following the method of Meyer and Harrison,[11] it is possible to calculate from the values given in Table 6 an isotope effect i, expressing the favoured loss of H over D from a carbon atom, and preference factors p_α and p_γ, reflecting the preference for loss of an α- and a γ-H(D) with respect to a β-H(D) respectively ($p_\beta = 1$). In the first instance the assumption was made that no exchange takes place between hydrogen and deuterium atoms of the alkyl group with the thiol hydrogen or deuterium. If the thiol H(D) atom is completely retained in the $H_xD_{2-x}S$ molecule the following expressions will hold for the intensity ratios of H_2S and HDS from the ions $c_3 - c_5$:

$$c_3: \quad [H_2S]/[HDS] = i(p_\alpha + 3p_\gamma)/2 = 6.13$$
$$c_4: \quad [H_2S]/[HDS] = ip_\alpha/(2 + 3p_\gamma) = 0.30$$
$$c_5: \quad [H_2S]/[HDS] = i(p_\alpha + 2)/3p_\gamma = 1.14$$

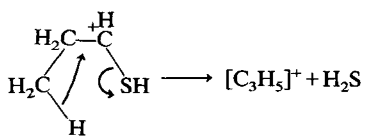
Solution of these equations gives $i = 1.90$, $p_\alpha = 1.16$ and $p_\gamma = 1.76$.

The assumption that no exchange takes place between alkyl H/D's and thiol H/D's cannot be completely correct, as ion c_3 also loses D_2S and this is only possible if exchange between an alkyl D and the thiol H has occurred. After the exchange, loss of HDS is still possible, but loss of H_2S is not. So HDS originates from ions with a –SH group as well as from ions with a –SD group.

It is now possible to make a correction for the contribution provided by the exchanged ions, assuming that the alkyl H/D's exchange with equal probability, independent of their position, with the thiol H/D atom. The fraction of –SD containing ions is called $6x$. Using the observed data for c_3, c_4 and c_5, approximate values for i, p_α, p_γ and x were obtained by iteration in this way. Convergence was reached after four iterations, leading to final values of $i = 2.32$, $p_\alpha = 1.07$, $p_\gamma = 1.91$ and $x = 1.67\%$. The values thus obtained correspond with loss of 0.13 α-, 0.25 β-, 0.72 γ- and 0.90 thiol hydrogens. If the hydrogen atoms of the alkyl group had been lost in a statistical way, the values would have been 0.18, 0.37, 0.55 and 0.90 respectively.

From the final values of i, p_α, p_γ and x, $[H_2S]/[HDS]$ ratios for ions c_6 and c_7 can be calculated. These are 93/7 and 91/9 respectively, and as can be seen from Table 6, a good correlation exists between calculated and measured ratios.

The data presented here point to preferential loss of γ-hydrogen atoms, indicating at least mainly a 5-membered transition state for loss of H_2S, when the reaction is a one-step process. This, together with the observed primary isotope effect, leads to a mechanism for H_2S loss as given in Scheme 7.



Scheme 7

Partial isomerization of ions c to d before loss of H_2S cannot *a priori* be excluded, but the observed peak for decomposition in the 1st FFR is narrow, Gaussian shaped and does not show any composite nature, so it is not likely that H_2S loss occurs along more than one reaction pathway. Complete isomerization to structure d is impossible, as this would make the β- and γ-hydrogen atoms of c identical, whereas a preference for loss of γ-hydrogens is observed. Therefore, the results are best rationalized by fragmentation from ions with structure c, preceded by incomplete hydrogen scrambling.

$[(CH_3)_2C{=}SH]^+$ (d). Table 7 lists the fractions for $H_xD_{2-x}S$ loss from the ions d_2 and d_3 in the 1st FFR. It is evident that the hydrogen atoms initially attached to sulfur appear for the greater part in the hydrogen sulfide molecule lost during fragmentation. It is clear also that some positional exchange between alkyl and thiol hydrogen atoms takes place, as ions d_2 and d_3 both lose some D_2S.

Since all H/D positions in the alkyl group are equivalent, no preference factors have to be used. It is easily calculated from the data in Table 7 that 20.5% of the thiol hydrogens have interchanged their position with an alkyl H/D and that an isotope effect $i = 2.2$ is operative. So of the two hydrogen atoms of H_2S, 0.8 originate from the –SH and 1.2 from the alkyl group.

The metastable peak for this reaction is broader

Table 7. Intensities[a] of the metastable transitions for loss of $H_xD_{2-x}S$ from ions *d*

Ion	Observed			Calculated[c]		
	H_2S	HDS	D_2S	H_2S	HDS	D_2S
d_2 $(CD_3)_2C{=}\overset{+}{S}H$	—	86	14	—	86	14
d_3 $CD_3(CH_3)C{=}\overset{+}{S}H$[b]	63	34	3	62	36	2

[a] The intensities are normalized to a total of 100% for each ion.
[b] Generated from $(CD_3)_2CH_3CSH$ or $(CH_3)_2CD_3CSH$.
[c] For the method of calculation of the expected intensities, see text.

than that for H_2S loss from *c*, but it is still narrow and Gaussian shaped. If the fragmenting ions again have structure *c*, rearrangements of *d* to *c* along one or more of the routes given in Scheme 4 are probable. The somewhat broader metastable peak may then be caused by an excess energy present in ions *c* formed from *d* in the rearrangement. This is only slightly reflected in the isotope effects observed for *c* and *d*. Contributions of mechanisms other than a 1,3-elimination from *c*, i.e. a 1,2-elimination, could also cause the difference, but the similarity of the metastable intensity ratios of *c* and *d* indicates that this cannot be a major effect.

$[CH_3CH{=}SCH_3]^+$ (a). Loss of hydrogen sulfide from ions of type *a* must necessarily be a complex reaction. The reaction requires rupture of both S—C bonds and formation of two S—H bonds. Table 8 lists the observed and calculated intensities of $H_xD_{2-x}S$ molecules lost from the deuterated ions a_3–a_5 in the 1st FFR. It is clear that extensive H/D scrambling for all hydrogen and deuterium atoms occurs prior to decomposition. The observed values may be compared with calculated intensities, assuming complete equivalence of all hydrogen and deuterium atoms (Table 8, model A). Obviously, there is no good correlation between calculated and observed intensities. For ions a_3 and a_4 loss of HDS is more intensive than expected for complete H/D scrambling. This cannot be caused entirely by an isotope effect, since for these ions the fraction of H_2S is less than expected for statistical distribution of all H and D atoms.

The data displayed in Table 8 point to an intermediate ion structure in which part of the deuterium atoms of ions a_3 and a_4 have migrated to the sulfur atom.

As was found for C_2H_4 loss from ions *a*, a rearrangement is proposed leading to structure *c*, from which loss of hydrogen sulfide takes place (Scheme 1). This rearrangement accounts for the pronounced loss of HDS from ions a_3 and a_4. Loss of H_2S from these ions is only possible after exchange of the alkyl hydrogen atoms with the thiol deuterium. As can be seen from Table 8, extensive exchange has taken place before fragmentation.

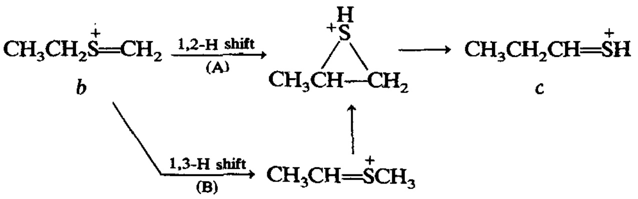
The observed intensities for loss of $H_xD_{2-x}S$ from the ions a_3–a_5 can now be correlated in the following way. As for ions with initial structure *c*, parameters p_α, p_γ and *i* are introduced for the ions *c*, formed from *a* via the cyclic intermediate *f*. Again the exchange of alkyl H/D atoms with thiol H/D atoms is assumed to be independent of their position and the percentage of exchange with each position is called *x*. For ion a_4 this gives after rearrangement:

$CH_3CHDCD{=}\overset{+}{S}D$ fraction: $100-4x$
$[HDS]/[D_2S]=i(1+3p_\gamma)/(p_\alpha+1)$
$CH_3CD_2CD{=}\overset{+}{S}H$ fraction: x
$[H_2S]/[HDS]=3ip_\gamma/(p_\alpha+2)$
$CH_2DCHDCD{=}S\overset{+}{H}$ fraction: $3x$
$[H_2S]/[HDS]=i(1+2p_\gamma)/(p_\alpha+1+p_\gamma)$

For ions a_3 and a_5 similar expressions can be derived in the same way. Calculation gives as best values: $p_\alpha=0.36$, $p_\gamma=1.27$, $i=1.80$ and $x=5\%$. This corresponds to the values given in Table 8, model B, for loss of $H_xD_{2-x}S$ and with an average loss of 0.80γ-, 0.42β-, 0.08α- and 0.70 thiol hydrogen atoms. As in case of ions directly formed as *c*, γ-hydrogen loss is again most prevalent. This suggests a contribution of the same mechanism for loss of hydrogen sulfide as proposed for ions with initial structure *c*.

After rearrangement of ions *a*, the ions *c* may be formed with excess energy. This may cause the somewhat lower isotope effect and the larger release of kinetic energy as compared with ions directly generated as *c*. The lower selectivity for 1,3-elimination may be caused by this effect, although differences in degree of H/D scrambling can also be the reason.

$[CH_2{=}SCH_2CH_3]^+$ (b). Table 9 presents the intensities for loss of $H_xD_{2-x}S$ from the labelled ions b_2–b_5 in the 1st FFR. As in the case of ions *a*, loss of H_2S from ions *b* must be a complex reaction. When the intensities for loss of $H_xD_{2-x}S$ from ion b_2 are compared with the corresponding values for ion a_3, a striking similarity is observed. This may indicate that prior to fragmentation, the ions a_3 and b_2 have rearranged to the intermediate structure *c* having the same label distribution. Two reaction pathways may lead to *c*, as given in Scheme 8. For ion b_2, both routes will lead to the same specifically labelled ion *c*. For the ions b_3–b_5, the two pathways will give differently



Scheme 8

Table 8. Intensities[a] of metastable transitions for the loss of $H_xD_{2-x}S$ from the ions with structure *a*

Ion	Observed			Calculated[c] A			B		
	H_2S	HDS	D_2S	H_2S	HDS	D_2S	H_2S	HDS	D_2S
a_3 $CH_3CD{=}\overset{+}{S}CD_3$	10	69	21	14	57	29	8	70	22
a_4 $CH_3CH{=}\overset{+}{S}CD_3$[b]	14	75	11	29	57	14	14	75	11
a_5 $CH_3CD{=}\overset{+}{S}CH_3$	85	15	—	71	29	—	86	14	—

[a] Normalized to a total of 100% for each type of ion.

[b] Identical results were obtained for ions generated from $CD_3SCH_2CH_3$ and $CD_3SCH(CH_3)_2$.

[c] For the method of calculation of the expected intensities for fragmentation according to models A and B see text.

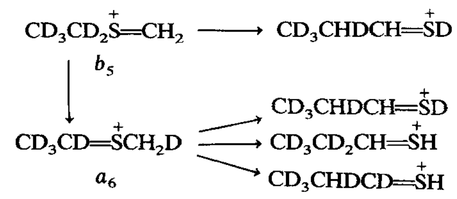
Table 9. Intensities[a] of the metastable transitions for loss of $H_xD_{2-x}S$ from ions with structure *b*

Ion	Observed			Calculated[b]								
				A			B			C		
	H_2S	HDS	D_2S	H_2S	HDS	D_2S	H_2S	HDS	D_2S	H_2S	HDS	D_2S
b_2 $CH_3CD_2\overset{+}{S}{=}CD_2$	9	71	20	8	70	22	8	70	22	8	70	22
b_3 $CH_3CD_2\overset{+}{S}{=}CH_2$	41	54	5	21	72	7	57	40	3	39	56	5
b_4 $CH_3CH_2\overset{+}{S}{=}CD_2$	57	41	2	78	21	1	40	56	4	59	39	2
b_5 $CD_3CD_2\overset{+}{S}{=}CH_2$	6	50	44	2	39	59	10	60	30	6	50	44

[a] The intensities are normalized to a total of 100% for each ion.

[b] For calculation of the expected intensities for pathways A, B and C, see text.

labelled fragmenting ions (Scheme 9); for instance for ion b_5 one may expect:



Scheme 9

With the set of parameters p_α, p_γ, i and x, calculated for ions of type *a*, it is possible to predict intensities for $H_xD_{2-x}S$ loss from type *b* ions. Table 9 presents the expected intensities calculated for pathways A and B (Scheme 8) respectively. Column C gives the calculated intensities when both routes participate equally in the formation of the fragmenting ion. This latter gives excellent agreement between observed and calculated intensities for all ions b_2–b_5. This indicates that both reaction pathways compete with equal efficiency in the formation of the fragmenting ions with structure *c*. The fragmentation routes proposed here for ions *b* are in agreement with the fact that many similarities are observed for ions *a* and *b*, i.e. identical metastable peak widths, isotope effects and preference factors.

CONCLUSIONS

^{13}C labelling experiments show that most $[C_3H_7S]^+$ ions are subject to complicated skeletal rearrangements leading to the ions (*c*) ($[CH_3CH_2CH{=}SH]^+$), before loss of C_2H_4 can occur. Ions with structure $[CH_3CH_2S{=}CH_2]^+$ (*b*) partially fragment directly. D labelling shows that also loss of H_2S most probably occurs from ions with structure *c* and that both fragmentations are preceded by extensive hydrogen exchange reactions. The latter processes can be described well by suitable models, but intrinsically these are only vague reflections of the complicated processes that really occur.

An improved insight into these isomerization and fragmentation reactions can be obtained when thermodynamic data for these ions become available. This will permit the construction of potential energy surfaces, as has been reported recently for other ions.[7,16]

EXPERIMENTAL

All measurements were performed on an AEI MS 902 double focusing mass spectrometer equipped with a variable β-slit, at an electron beam energy of 70 eV. The source temperature was 130 °C. Samples were introduced via an all glass heated inlet system with a temperature of 120 °C. Fragmentation reactions in the first drift region were observed by means of the refocusing technique.[17] All metastable intensities in this paper are the average of at least three measurements. When necessary, corrections were made for incomplete labelling. The label content of the compounds was determined by mass spectrometry at low electron energy. Metastable peak widths were measured on a Vacuum Generators ZAB-2F instrument. The purity of all compounds used for this study was checked by GLC or HPLC. The position of the deuterium labels was ascertained by NMR spectroscopy.

The preparation of 2-propanethiol-2-[^{13}C] and 1,2-bis-(thiomethoxy[^{13}C])ethane has been described elsewhere.[8] The labelled iodides used in the following syntheses were either commercially available (C_2D_5I) or synthesized via a simple procedure described earlier.[1]

***t*-Butyl mercaptan-*d*$_3$.** A solution of CD_3I (16 g) in ether (50 ml) was added in a N_2 atmosphere to Mg turnings (4 g). After the reaction had ceased, the grey liquid was filtered and acetone (8.8 g) in ether (50 ml) was added under gentle reflux. The heating was continued for another 0.5 h. After cooling, water (20 ml) and a concentrated NH_4Cl solution (40 ml) were added subsequently. The two layers were separated and the water layer was extracted with two portions of 50 ml ether. The combined organic layers were dried over Na_2SO_4, filtered and distilled. Of the *t*-butanol-*d*$_3$ so formed, the fraction with b.p. 80–82 °C was used for further reactions.

t-Butanol-*d*$_3$ (6.1 g) was shaken with conc. hydrochloric acid (17 ml) for 20 min. The chloride layer was separated and washed with water and a 10% $NaHCO_3$ solution. The chloride was dried on $MgSO_4$ and used without further purification.

t-Butylchloride-*d*$_3$ (8 g) in dry ether (25 ml) was added to Mg turnings (3.5 g) in ether (15 ml) in a N_2 atmosphere. When all the chloride was added, heating was continued for 0.5 h. The solution was filtered and sulfur (2.0 g, recrystallized from CS_2) was added in small portions under vigorous agitation. The yellow solution was heated for another 0.5 h, cooled and treated with water (20 ml) and a concentrated NH_4Cl solution (40 ml). The two layers were separated, the water layer was extracted twice with 50 ml ether, the combined ether layers were dried over Na_2SO_4 and distilled. The *t*-butyl mercaptan-d_3 was finally purified by GLC, using a combination of SE 30 and LAC columns. The isotopic purity was: d_3: 97.5%, d_2: 2.5%.

***t*-Butyl mercaptan d_6.** In the same way as described above *t*-butyl mercaptan-d_6 was prepared from methylmagnesium iodide and acetone-d_6. Isotopic purity: d_6 94.5%, d_5 5,3%, d_4 0.2%.

The deuterated 3-pentanethiols were made by the following general procedure from labelled 3-pentanones.

3-Pentanethiol.[18] 3-Pentanone was converted into its dithioacetal by reaction with $ZnCl_2$ and excess CH_3SH.[18]

In a typical experiment Na (1.4 g) was dissolved in liquid NH_3 (50 ml). Subsequently the dithioacetal (2.5 g) was added. After stirring for 0.5 h at −40 °C, the blue colour had vanished. The NH_3 was evaporated and water (30 ml) and *n*-pentane (50 ml) were added. The thiol was liberated by adding a solution of 20% H_2SO_4 (30 ml), cooled to −20 °C to the reaction mixture. The pentane layer was separated from the water layer, which was extracted with two portions of 25 ml pentane. The combined organic layers were dried on $MgSO_4$, filtered and distilled. When necessary the 3-pentanethiols were purified by preparative GLC using a squalane column.

3-Pentanone-1,1,1,2,2-d_5. 3-Pentanol-1,1,1,2,2-d_5 was made by reaction of the Grignard reagent of ethyl bromide-d_5 with propionaldehyde.[19]

The alcohol (7.3 g) was dissolved in ether (30 ml) and cooled to 5 °C. A solution of $Na_2Cr_2O_7.2H_2O$ (7.8 g) and conc. H_2SO_4 (10.3 g) in water (30 ml) was added dropwise in 0.5 h. Stirring was continued for another 2 h at room temperature. The ether layer was separated, washed with two portions of 25 ml water and twice with 25 ml of a 10% $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and distilled. The fraction with a boiling range of 101–103 °C was used. NMR spectroscopy showed that no exchange of deuterium and hydrogen had occurred during the reaction.

3-Pentanone-1,1,1-d_3 and **3-pentanone-2,2,4,4-d_4.** Part of the d_5 labelled ketone was converted into its d_3 analogue by repeated exchange with H_2O and K_2CO_3.[20] 3-Pentanone-2,2,4,4-d_4 was obtained in a similar way by repeated exchange of 3-pentanone with D_2O and K_2CO_3.[20]

3-Pentanethiol-3-d_1. This compound was synthesized by reduction of the dithioacetal of 3-pentanone in liquid ND_3 obtained by reaction of D_2O and Mg_3N_2.[21]

The isotopic purity of the labelled 3-pentanethiols was:

3-Pentanethiol-1,1,1,2,2-d_5:	d_5 96.8%, d_4 3.2%
3-Pentanethiol-2,2,4,4-d_4:	d_4 97.1%, d_3 2.9%
3-Pentanethiol-1,1,1-d_3:	d_4 2.1%, d_3 97.9%
3-Pentanethiol-3-d_1:	d_1 44.0%, d_0 56.0%

3-Pentanethiol-3-[^{13}C] and **2-pentanethiol-3-[^{13}C].** Formic acid-[^{13}C] (1 g) in ether (10 ml) was cooled to −20 °C and treated with a slight excess of a solution of CH_2N_2 in ether. The solution was dried over $MgSO_4$ and distilled. The distillate, being a mixture of methyl formate and ether was collected at −30 °C. The cold mixture was added under gentle reflux to a solution of EtMgI, obtained from C_2H_5I (9.5 g) and Mg turnings (5 g). Heating was continued for an additional 2 h. Water (10 ml) and concentrated NH_4Cl solution (20 ml) were added subsequently. The layers were separated and the water layer was extracted with three portions of 20 ml ether. The ether layers were dried over $MgSO_4$ and distilled. The 3-pentanol-3-[^{13}C] so formed was converted into a mixture of the two mercaptans by reaction with 67% HI solution and thiourea.[8] Separation of the isomeric thiols was achieved by preparative HPLC using a Si-60 column (particle size 5 μ) and *n*-pentane as the solvent. The ^{13}C label content was 90%.

1,2-bis-Thioethoxyethane-[1,2-bis-^{13}C]. A mixture of 1,2-dibromoethane-[1,2-bis-^{13}C] (0.5 g) and C_2H_5SNa (0.44 g) in water (5 ml) was heated under reflux for 2 h. The product was separated from the water layer, dried over $MgSO_4$, and used without further purification. The isotopic purity was: 2 ^{13}C 80%, 1 ^{13}C 18.6%, 0 ^{13}C 1.4%.

Diethylsulfide-$\alpha,\alpha,\beta,\beta,\beta$-$d_5$. Ethyliodide-$d_5$ (0.7 g) was heated under reflux with C_2H_5SNa (0.37 g) in water (5 ml). After separation and drying over $MgSO_4$, the sulfide was used without further purification.

Diethylsulfide-$\alpha,\alpha,\alpha'\alpha'$-$d_4$ and **ethyl-α,α-d_2-*n*-propylsulfide** were prepared as described above by reaction of ethyliodide-1,1-d_2 (1.1 g) with Na_2S (0.86 g) and $CH_3CH_2CH_2SNa$ (0.7 g) respectively. The label contents were:

Diethylsulfide-$\alpha,\alpha,\beta,\beta,\beta$-$d_5$:	d_5 96.4%, d_4 3.5%, d_3 0.1%
Diethylsulfide-$\alpha,\alpha,\alpha'\alpha'$-$d_4$:	d_4 97.5%, d_3 2.5%
Ethyl-α,α-d_2-*n*-propylsulfide:	d_2 98.0%, d_1 2.0%

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