probability that it will be found on the oxygen atoms of the methoxy groups. This is contrary to the expectation that VB structures like V should contribute substantially to the resonance hybrid for this molecule.[2]

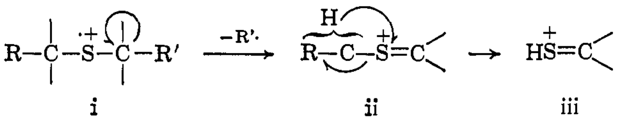
There is also interest in examining the distribution of unshared electron pairs in these systems. Wave functions obtained with the "optimum" parameters (which used $\varphi = 0°$, and $\tau = 27°$) include one in which an electron pair has a high probability ($\rho_{13} = 0.100$, $\rho_{14} = 0.185$) that it will be on atoms 13 and 14, and is otherwise distributed among the *ortho* and *para* positions of all three aromatic rings. A strongly bonding MO contains one electron pair fully localized on AO no. 27. These results are not changed by either type of substitution studied. Somewhat different results are obtained when $\varphi = 45°$. The unpaired electron distribution is essentially unchanged, with some increase in density at atoms 13 and 14, at the expense of density on the nitro groups in the picryl ring. An unshared electron pair has substantial probabilities in AO no. 14 and 27, with distribution otherwise to *ortho* and *para* positions of all three rings. A strongly bonding MO has nearly half of the electron density in position 27, and the remainder in the picryl ring. These distributions are not greatly affected by substitution.

Mass Spectrometry in Structural and Stereochemical Problems. CIV.[1] The Nature of the Cyclic Transition State in Hydrogen Rearrangements of Aliphatic Sulfides[2]

Shelia Sample[3] and Carl Djerassi

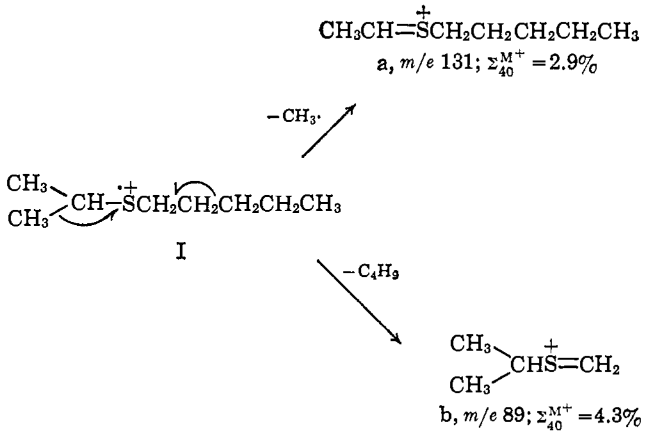
Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received December 22, 1965*

Abstract: Levy and Stahl[4] first studied the fragmentation of thioethers and concluded that the spectra were dominated by fragments arising from α cleavage, carbon–sulfur cleavage, and olefin elimination forming mercaptan ions. A fourth type of fragmentation, characteristic of ethers and amines, is also found and is represented below for the sulfur case. Through deuterium-labeling experiments, it has now been demonstrated that the hydrogen transfer to sulfur (ii → iii) is not just a four-centered process as had been originally postulated[5] for formation of the analogous fragment in ethers. Rather as had been shown recently with labeled ethers[6a] and amines,[6b] four-, five-, and six-membered cyclic transition states transferring secondary hydrogen to sulfur are equally favored. However, if a choice between secondary and primary hydrogen is available, transfer of the former predominates. Other features of the mass spectra of aliphatic sulfides, including those observed by Levy and Stahl,[4] are discussed in terms of deuterated analogs.



A preliminary study of the fragmentation of thioethers upon electron bombardment was made by Levy and Stahl[4] in 1961. They observed that the spectra were dominated by fragments arising from α cleavage, carbon–sulfur bond cleavage, and olefin elimination to form mercaptan ions.

The first of these processes, α fission, is also important in the fragmentation of ethers[5,6a] and amines.[6b,7] Its counterpart in sulfides can be illustrated by the mass spectrum (Figure 1) of isopropyl *n*-amyl sulfide (I). It should be noted that the usual mass spectrometric generalization holds, namely, that the more highly substituted radical is lost preferentially.[5,8] However,



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[1] Paper CIII: C. Djerassi, A. M. Duffield, F. Komitsky, Jr., and L. Tökes, *J. Am. Chem. Soc.*, **88**, 860 (1966).

[2] Financial support (Grant No. AM-04257) by the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible by NASA Grant NsG 81-60.

[3] Recipient of National Science Foundation (1963–1965) and National Institutes of Health (1965–1966) predoctoral fellowships.

[4] E. J. Levy and W. A. Stahl, *Anal. Chem.*, **33**, 707 (1961).

[5] F. W. McLafferty, *ibid.*, **29**, 1782 (1957).

[6] (a) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5747 (1965); (b) C. Djerassi and C. Fenselau, *ibid.*, **87**, 5752 (1965).

[7] R. S. Gohlke and F. W. McLafferty, *ibid.*, **34**, 1281 (1962).

[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp 50–52.

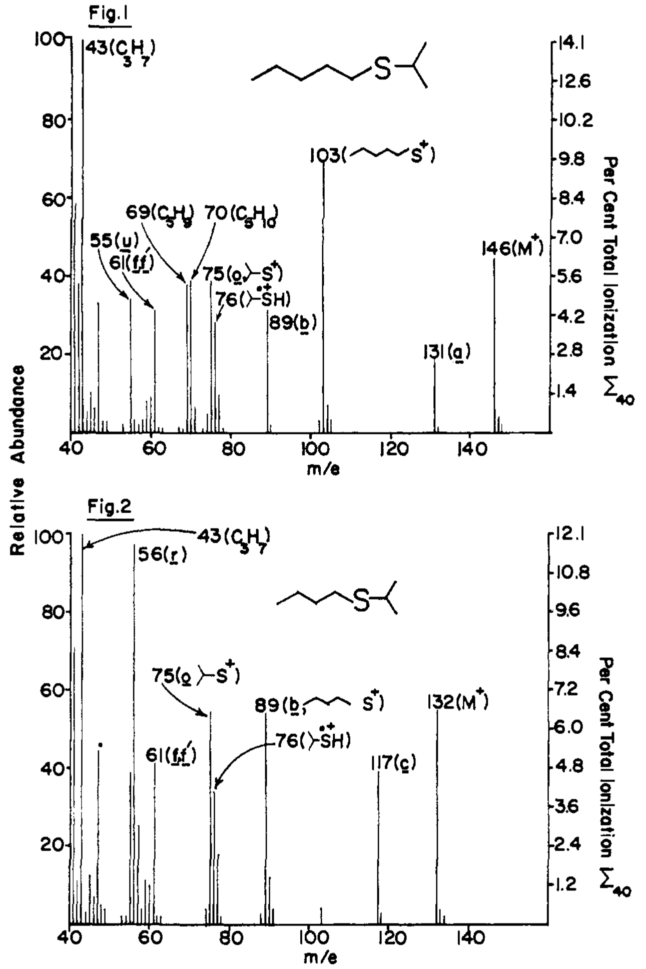
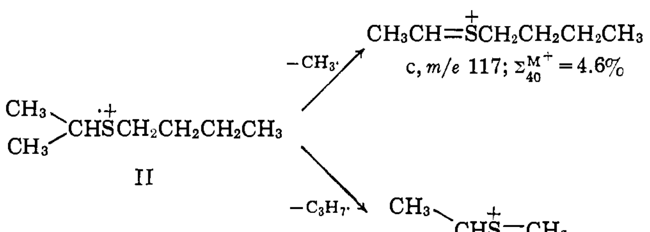


Figure 1. Mass spectrum of isopropyl *n*-amyl sulfide (I).
Figure 2. Mass spectrum of isopropyl *n*-butyl sulfide (II).

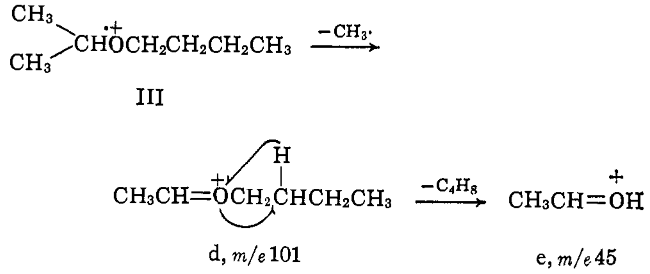
branching at the site of α fission can enhance cleavage at that point to the extent that in the mass spectrum (Figure 2) of isopropyl *n*-butyl sulfide (II), loss of propyl (II → b) and loss of the isopropyl methyl group (II → c) occur in nearly equal amounts.[9]



$$\mathrm{(CH_3)_2CH\overset{\cdot+}{S}CH_2CH_2CH_2CH_3}\ \text{II} \xrightarrow{-CH_3\cdot} \mathrm{CH_3CH{=}\overset{+}{S}CH_2CH_2CH_2CH_3}\quad \text{c, } m/e\ 117;\ \Sigma_{40}^{M^+} = 4.6\%$$

$$\mathrm{(CH_3)_2CH\overset{\cdot+}{S}CH_2CH_2CH_2CH_3}\ \text{II} \xrightarrow{-C_3H_7\cdot} \mathrm{(CH_3)_2CH\overset{+}{S}{=}CH_2}\quad \text{b, } m/e\ 89;\ \Sigma_{40}^{M^+} = 4.7\%$$

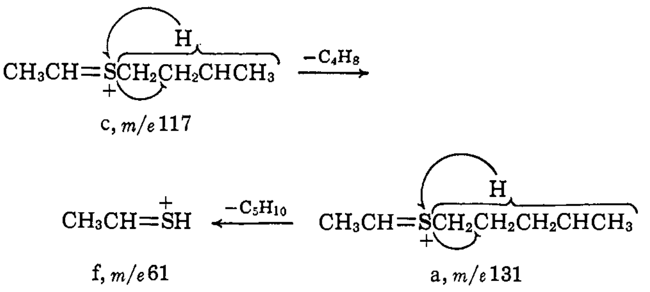
More interesting than the formation of these α-cleavage ions is their subsequent decomposition. Of particular pertinence is the fact that the fragment $>C{=}XH^+$ (X = O, NR, or S) present in the spectra of ethers[5] and amines[7] is also present in the spectra of thioethers.[4] McLafferty[5] first postulated a mechanism for its formation in ethers from an α-cleavage product by transfer of hydrogen through a four-centered transition state. In point of fact, this hydrogen transfer (d → e) proceeds through various sized (three- four-, five-, and six-membered) transition states in ethers[6a] and amines;[6b] therefore, it was of interest to study the sulfur analog to examine the influence of this heteroatom on the preferred size of the transition state. Also, since no deuterium labeling had so far been performed among sulfides, generalizations about their fragmentation pattern could be obtained from such a study.



$$\mathrm{(CH_3)_2CH\overset{\cdot+}{O}CH_2CH_2CH_2CH_3}\ \text{III} \xrightarrow{-CH_3\cdot}$$

$$\mathrm{CH_3CH{=}\overset{+}{O}CH_2CHCH_2CH_3}\ (\text{d, } m/e\,101) \xrightarrow{-C_4H_8} \mathrm{CH_3CH{=}\overset{+}{O}H}\ (\text{e, } m/e\,45)$$

Isopropyl *n*-butyl (II) and *n*-amyl (I) sulfides were chosen as models, since their oxygen counterparts had been studied[6a] earlier. The very reaction for an examination of the preferred transition state (if any)[10] in sulfides is the genesis of ion f (m/e 61) from the α-cleavage products a and c. Upon measuring the spectra of compounds having each carbon of the butyl and pentyl side chains labeled with deuterium, it was possible to calculate the amount transferred from each position in this process. The data obtained, together with the earlier results from ethers and amines, are summarized in Table I. The origin of the transferred hydrogen is quite similar to that observed in ethers[7a] and amines[6b] and leads to two generalizations. First, migration of secondary hydrogen is preferred over migration of primary hydrogen. Thus, the amount of hydrogen originating from the δ position rises significantly (see Table I) when it is secondary as in the pentyl series. Second, all factors being equal (see I in Table I) four-, five-, and six-membered transition states are equally favored, but smaller (three-membered) and larger (seven-membered) ring sizes are also feasible.



$$\mathrm{CH_3CH{=}\overset{+}{S}CH_2CH_2CHCH_3}\ (\text{c, } m/e\,117) \xrightarrow{-C_4H_8}$$

$$\mathrm{CH_3CH{=}\overset{+}{S}H}\ (\text{f, } m/e\,61) \xleftarrow{-C_5H_{10}} \mathrm{CH_3CH{=}\overset{+}{S}CH_2CH_2CH_2CHCH_3}\ (\text{a, } m/e\,131)$$

However, the deuterium-labeling results (see Tables III and IV) indicate that in thioethers the species f (m/e 61) is also formed by an alternate pathway which is absent in ethers[6a] and just beginning to appear in amines.[6b] This process is initiated by β cleavage (II → g) and is responsible for 27% of m/e 61 (f') in both the isopropyl *n*-butyl and *n*-amyl sulfides. Such β cleavage has a precedent in the fragmentation of cyclic sulfides since it was shown[11] that 35% of the

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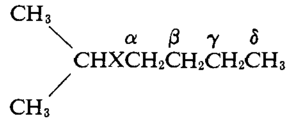
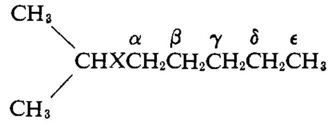
[9] This may not be obvious from simple inspection of the spectrum; however, 32% of m/e 89 is formed by simple carbon–sulfur cleavage (see Table III).

[10] In fact, a four-centered transition state in sulfides has been accepted (D. C. DeJongh, *J. Org. Chem.*, 30, 453 (1965)) by analogy to the earlier work.

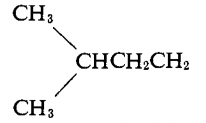
[11] A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 2920 (1965).

Table I. Source of Hydrogen Transferred from Butyl and Pentyl Chains in Production of $CH_3CH{=}XH^+$ (X = O, S, NCH_3) Ion from α-Cleavage Fragments

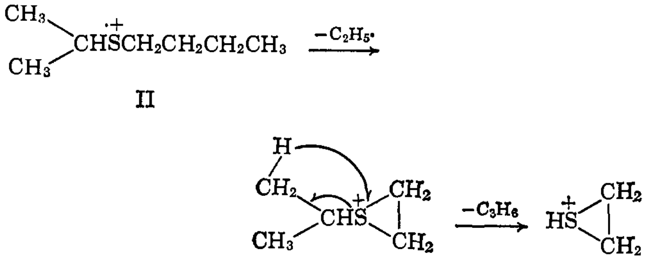
Compd	Position labeled	% hydrogen transfer X = S	X = O[a]	X = NCH_3[b]
 II				
	α	15	16	10–26
	β	31	35	21–25
	γ	36	40	23
	δ	15	2–9	17
 I				
	α	10	10	14–18
	β	25	26	22–26
	γ	28	25	19
	δ	28	29	20
	ε	6	1–10	6

[a] See ref 7a. [b] See ref 7b.

Table II. Direction of Carbon–Sulfur Cleavage in Unsymmetrical Sulfides

Substance (RSR') R	R'	Total ionization Σ_{40}^{M+} of fragment R	R'
$CH_3CH_2CH_2CH_2CH_2$ (m/e 103)	 (m/e 103)	2.9	0.7
$(CH_3)_2CH$ (m/e 75)	$CH_3CH_2CH_2CH_2$ (m/e 89)	1.6	2.1
$(CH_3)_2CH$ (m/e 75)	$CH_3CH_2CH_2CH_2CH_2$ (m/e 103)	1.5	9.7
CH_2CH_2 (m/e 61)	$CH_3CH_2CH_2CH_2CH_2CH_2$ (m/e 117)	0	9.7

M − 1 peak of tetrahydrothiophene arises from β rather than α elimination of a hydrogen atom.



II

g, m/e 131

f', m/e 61

Since formation of this β-cleavage species f' involves a hydrogen transfer, it was of interest to prepare a compound in which such β fission would be favored and to determine the specificity of this hydrogen rearrangement. n-Amyl isoamyl sulfide (IV; see Figure 3) was chosen for this purpose since the isopropyl group at the β position should favor β fission. In fact, when the α position of the isoamyl chain was labeled with deuterium (IVb), the peak was entirely shifted to m/e 63 (i).

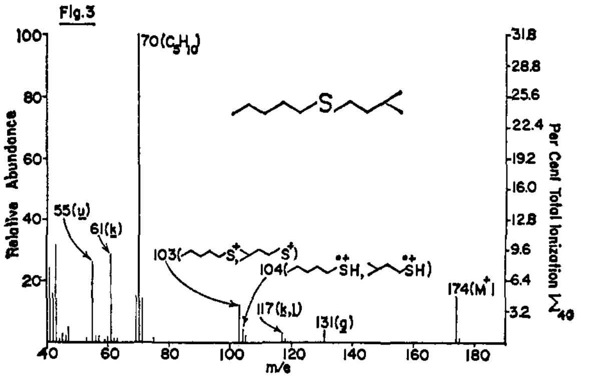
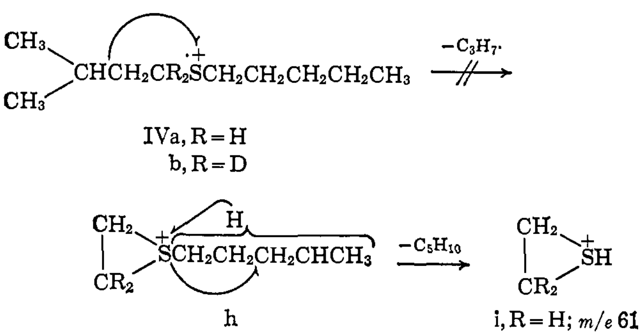


Figure 3. Mass spectrum of n-amyl isoamyl sulfide (IV).

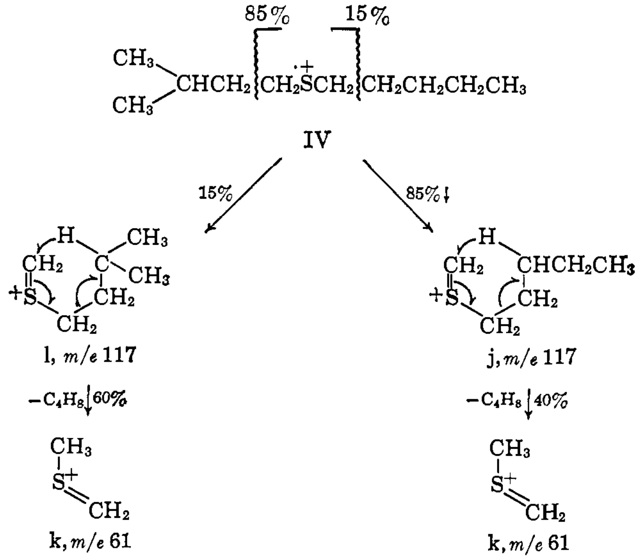


IVa, R = H
b, R = D

h

i, R = H; m/e 61
R = D; m/e 63

However, when the spectra of analogs of IV labeled in the n-amyl chain were measured (see Table V) it became apparent that the above outlined mechanism (IV → h → i) was not operating in the formation of the m/e 61 species in n-amyl isoamyl sulfide (IV). Instead, α cleavage followed by a McLafferty rearrangement involving the γ hydrogen of the remaining chain gives rise to this peak. This was further substantiated by labeling the isoamyl γ position with deuterium and observing (Table V) partial shift of the peak to m/e 62. The relative amounts of the peak derived from each side chain are indicated in the above flow sheet.



IV

l, m/e 117

j, m/e 117

k, m/e 61

k, m/e 61

Table III. Principal Peaks in the Mass Spectra of Isopropyl *n*-Butyl Sulfide and Its Deuterated Analogs[a]

Compd	Isotopic purity, %	Peaks, *m/e* (%) M − 15	M − 43	M − 56	M − 57
$(CH_3)_2CHSCH_2CH_2CH_2CH_3$ II		117	89	76	75
$(CH_3)_2CHSCD_2CH_2CH_2CH_3$ VIII	99 d_2 1 d_1	119 q	91 q	76	75 (25) 77 (75)
$(CH_3)_2CHSCH_2CD_2CH_2CH_3$ IX	97 d_2 3 d_1	119 q	89 (68) 91 (32)	76 (<55) 77 (>45)	75
$(CH_3)_2CHSCH_2CH_2CD_2CH_3$ X	95 d_2 5 d_1	119 q	89 (68) 91 (32)	76 (<85) 7 (>15)	75 (25) 76 (75)
$(CH_3)_2CHSCH_2CH_2CH_2CD_3$ XI	98 d_3 2 d_2	120 q	89 (68) 92 (32)	76	75
$(CH_3)_2CDSCH_2CH_2CH_2CH_3$ XII	100 d_1	118 q	89 (32) 90 (68)	77q	76 q
$(CD_3)_2CHSCH_2CH_2CH_2CH_3$ XIII	91 d_6 9 d_5	120 q	89 (32) 95 (68)	82 q	78 (75) 81 (25)

[a] The symbol q denotes a quantitative transfer (>95%). An uncertainty of ±5% is estimated in the calculations of all peaks of greater than 20% relative abundance.

Table IV. Principal Peaks in the Mass Spectra of Pentyl Isopropyl Sulfide and Its Deuterated Analogs[a,b]

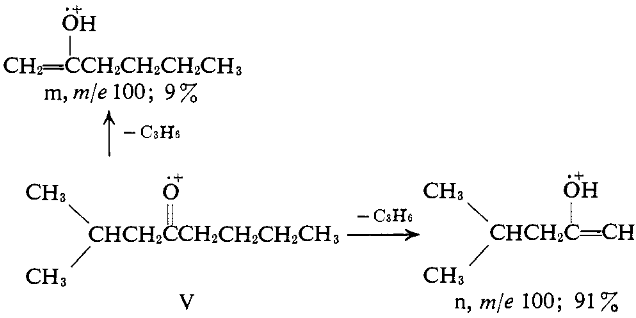
Compd	Isotopic purity, %	Peaks, *m/e* (%) M − 15	M − 43	M − 57	M − 70	M − 71	M − 77	M − 91
$CH_3CH_2CH_2CH_2CH_2SCH(CH_3)_2$ I		131	103	89	76	75	69 71 q	55
$CH_3CH_2CH_2CH_2CD_2SCH(CH_3)_2$ XIV	96 d_2 4 d_1	133 q	105 q	91 q	76	75 (25) 77 (75)		55 (25) 57 (75)
$CH_3CH_2CH_2CD_2CH_2SCH(CH_3)_2$ XV	75 d_2 25 d_1	133 q	105 q	89	76 (<67) 77 (>33)	75		
$CH_3CH_2CD_2CH_2CH_2SCH(CH_3)_2$ XVI	95 d_2 5 d_1	133 q	105 q	89	76 (<87) 77 (>15)	75 (25) 76 (75)		
$CH_3CD_2CH_2CH_2CH_2SCH(CH_3)_2$ XVII	96 d_2 4 d_1	133 q	105 q	89	76	75		
$CD_3CH_2CH_2CH_2CH_2SCH(CH_3)_2$ XVIII	96 d_3 4 d_2	134 q	106 q	89	76	75		55 (75) 57 (25)
$CH_3CH_2CH_2CH_2CH_2SCH(CD_3)_2$ XIX	79 d_6 21 d_5	134 q	103	95 q	82 q	78 (75) 81 (25)	69	

[a] See footnote *a* in Table III. [b] Blank spaces indicate that the complexity of the peak group in these labeled analogs rendered calculation of the shifts impossible.

Further confirmation for the operation of the McLafferty rearrangement is provided by the presence of the appropriate metastable peak at *m/e* 31.9 (calcd $61^2/117 = 31.8$).[12]

Three factors operate here to equalize the relative amounts of *m/e* 61 (k) coming from each alkyl chain. Even though a primary radical is formed in either case by α fission, that radical possessing a branched chain is lost preferentially, thus leading predominantly (85%) to species j. Furthermore, a McLafferty rearrangement from this fragment j ought to be favored over that from l on a statistical basis, since it has twice as many γ hydrogens. However, on the other hand, this process (j → k) is less favorable than l → k since the hydrogen transferred is secondary rather than tertiary. In fact, calculations using the above data show that in this McLafferty rearrangement, the magnitude of the preference for migration of a hydrogen from a tertiary position over migration from a secondary position is 17:1.

This result is not unexpected as it had been previously[13] shown that in unsymmetric ketones such as V, the intensity of the McLafferty rearrangement peak resulting from transfer of a secondary hydrogen (n) is greater than that resulting from transfer of primary hydrogen (m) by the following amounts.



m, *m/e* 100; 9%

V

n, *m/e* 100; 91%

α Cleavage followed by McLafferty rearrangement is also discernible in the spectra of isopropyl *n*-butyl (Figure 2) and *n*-amyl (Figure 1) sulfide and is responsible for 75% of the *m/e* 75 peak (o) in both cases. Observation of the appropriate metastable ions[12] in the isopropyl *n*-butyl (48.0; calcd for $75^2/117 = 48.0$) and *n*-amyl (43.1; calcd for $75^2/131 = 43.1$) sulfides confirms that such a two-step mechanism is operating.

McLafferty rearrangements in sulfides may not be limited to those of the α-cleavage products. The Spitellers[14] pointed out that the hydrocarbon ion of

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[12] All metastable peaks were determined by means of the logarithmic transfer recorder developed recently in these laboratories: R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, *Anal. Chem.*, 37, 776 (1965).

[13] H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, 22, 1391 (1966).

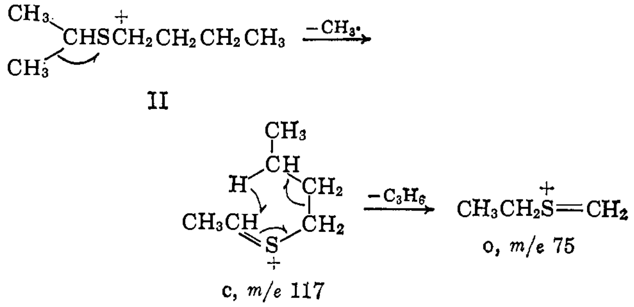
[14] G. Spiteller and M. Spiteller-Friedman, *Monatsh.*, 95, 257 (1964).

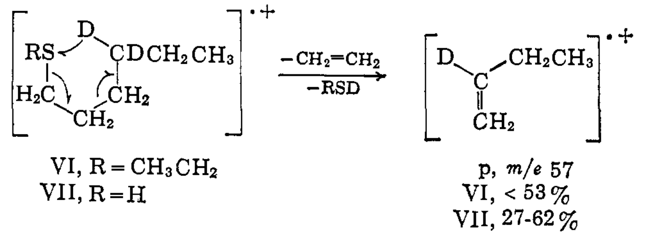
Table V. Principal Peaks in the Mass Spectra of *n*-Amyl Isoamyl Sulfide (Figure 3) and Its Deuterated Analogs[a,b]

		Peaks, m/e (%)									
Compd	Isotopic purity, %	M − 43	M − 57	M − 69	M − 70	M − 71	M − 103	M − 104	M − 105	M − 113	M − 119
$(CH_3)_2CHCH_2CH_2SCH_2CH_2CH_2CH_2CH_3$ IV		131	117	105	104	103	71	70	69	61	55
$(CH_3)_2CHCH_2CH_2SCD_2CH_2CH_2CH_2CH_3$ XX	99 d_2 1 d_1	133 q	119 q	105 (75) 107 (25)	104 (25) 106 (75)	103 (25) 105 (75)	71 (55) 73 (45)	70 (80) 72 (20)	69 (30) 71 (70)	63 q	55 (85) 56–57 (15)
$(CH_3)_2CHCH_2CH_2SCH_2CD_2CH_2CH_2CH_3$ XXI	71 d_2 29 d_1	133 q	117 (15) 119 (85)					70 (80) 71–72 (20)		61	55 (85) 56–57 (15)
$(CH_3)_2CHCH_2CH_2SCH_2CH_2CD_2CH_2CH_3$ XXII	94 d_2 6 d_1	133 q	117 (15) 119 (85)					70 (80) 71–72 (20)		61 (60) 62 (40)	55 (85) 56–57 (15)
$(CH_3)_2CHCH_2CH_2SCH_2CH_2CH_2CD_2CH_3$ XXIII	93 d_2 7 d_1	133 q	117 (15) 119 (85)					70 (80) 71–72 (20)		61	55 (85) 56–57 (15)
$(CH_3)_2CHCH_2CH_2SCH_2CH_2CH_2CH_2CD_3$ XXIV	96 d_3 1 d_2 3 d_1	134 q	117 (15) 120 (85)	105 (75) 108 (25)	104 (75) 107 (25)	103 (25) 106 (75)		70 (80) 71–72 (20)		61	55 (85) 56–57 (15)
$(CH_3)_2CHCH_2CD_2SCH_2CH_2CH_2CH_2CH_3$ XXV	99 d_2 1 d_1	133 q	119 q	105 (25) 107 (75)	104 (25) 106 (75)	103 (75) 105 (25)	71 (45) 73 (55)	70 (20) 72 (80)	69 (70) 71 (30)	63 q	55 (30) 56–57 (70)
$(CH_3)_2CDCH_2CH_2SCH_2CH_2CH_2CH_2CH_3$ XXVI	99 d_1 1 d_0	131	117 (85) 118 (15)							61 (40) 62 (60)	55 (80) 56 (20)

[a,b] See corresponding footnotes in Tables III and IV.

mass 56 in ethyl *n*-hexyl sulfide (VI, Figure 4) could arise from a McLafferty rearrangement of hydrogen to sulfur through a six-membered transition state. An analogous peak could also be operative in the corresponding mercaptan (VII). We were interested in determining whether this postulated transformation proceeds with the site specificity characteristic of the McLafferty rearrangement. When the δ hydrogen of the mercaptan and sulfide were labeled with deuterium, the percentage of the original peak intensity that moved to *m/e* 57 (p) in VI and VII is indicated under structure p. The results show that the type of McLafferty rearrangement proposed by the Spitellers[14] probably occurs to the extent of less than 50%. Hence this process cannot be compared to the completely site-specific McLafferty rearrangement encountered in carbonyl compounds.[13]





The charge can also be retained on a mercaptan fragment which is formed by elimination of an olefin from the molecular ion. Peaks corresponding to ethyl (*m/e* 62 in Figure 4), isopropyl (*m/e* 76 in Figures 1 and 2), *n*-amyl and isoamyl (*m/e* 104 in Figure 3) mercaptan were observed in the spectra studied. It is striking that in the spectra of isopropyl *n*-butyl (Figure 2), isopropyl *n*-amyl (Figure 1), and ethyl *n*-hexyl sulfide (Figure 4), little or no peak corresponding to *n*-butyl (*m/e* 90), *n*-amyl (*m/e* 104), or *n*-hexyl (*m/e* 118) mercaptan fragments is observed. This reflects a preference for loss of the higher molecular weight olefin. Branched olefins are lost to a greater degree than unbranched ones as indicated by the 3:1 ratio favoring loss of isopentene over loss of *n*-pentene in *n*-amyl isoamyl sulfide (see Table V).

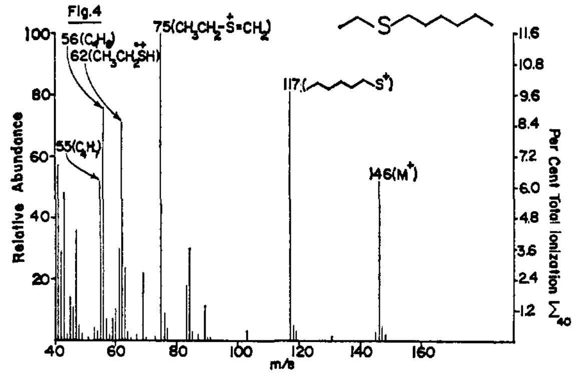
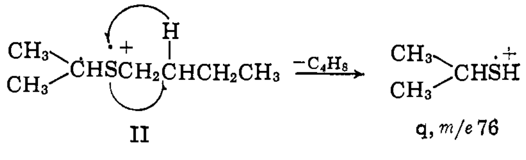


Figure 4. Mass spectrum of ethyl *n*-hexyl sulfide (VI).

As judged from the data collected in Tables III and IV, the hydrogen transferred to sulfur in the greatest amount in mercaptan fragment (q) formation appears to be the one from the β position. Labeling the δ position of the ethyl *n*-hexyl sulfide, however, shows that a six-membered elimination can also occur to the extent of about 20% when the chain is sufficiently long.

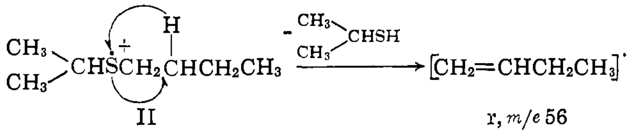


Levy and Stahl[4] observed prevalent carbon–sulfur cleavage fragments in thioether spectra, although ethers[5,6a] and amines[6b,7] exhibit carbon–heteroatom cleavage only to a small extent. Table II lists these fragments as well as their percentage of the total ionization Σ_{40}^{M+} in the compounds studied. The only apparent conclusion that can be drawn from these data is that as the difference in chain length of the two fragments becomes greater, there is a greater preference for carbon–sulfur cleavage with charge retention on the longer alkyl chain.

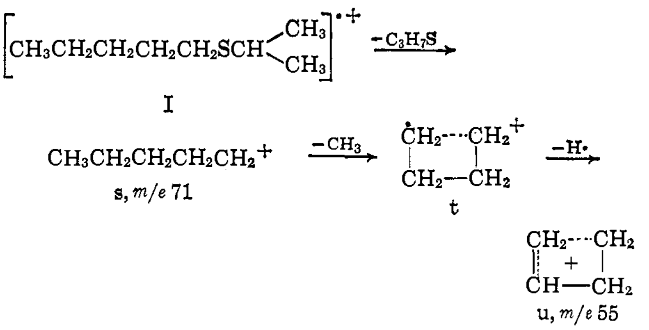
The only remaining peaks of importance are the ubiquitous hydrocarbon fragments which are absent in amines.[6b] When formed in the spectra of ethers,[6a] they generally appear as one peak corresponding to the entire saturated chain. However, in thioethers (*e.g.*, Figure 2) the initial hydrocarbon peak group consists of fragments corresponding to the saturated carbonium ion (*m*/*e* 57), the corresponding olefin ion radical (*m*/*e* 56), and the allyl ion (*m*/*e* 55). Removal of one carbon at a time throughout the remainder of the low mass range gives rise to a homologous series of allyl ions at 14-mass-unit intervals.

The formation of these hydrocarbon fragments is accompanied by substantial deuterium scrambling of a hitherto unobserved type. It is especially striking that in the spectrum of isopropyl *n*-butyl sulfide, the *m*/*e* 56 peak ($C_4H_8^{\cdot +}$) is separated into *m*/*e* 56 and *m*/*e* 57 ($C_4H_7D^{\cdot +}$) when the methyl hydrogens of the isopropyl chain are labeled with deuterium. Measurement of the spectrum of isopropyl *n*-perdeuteriobutyl sulfide also showed the presence of peaks corresponding to four-carbon fragments containing one hydrogen at *m*/*e* 63 (C_4D_7H) and *m*/*e* 65 (C_4HD_8). The type of scrambling encountered evidentally involves "jumping" of hydrogen (or deuterium) from one alkyl chain to the other.

In spite of the hydrogen or deuterium scrambling, it is possible to draw some conclusions about the mode of formation of these hydrocarbon species. The saturated hydrocarbon ions are probably formed by simple carbon–sulfur cleavage with charge retention on the hydrocarbon fragment. In fact, *m*/*e* 43 ($C_3H_7^+$), formed in this manner, is the base peak in the spectra (Figures 1 and 2) of the isopropyl sulfides. Olefinic fragments can be formed from these species by loss of a hydrogen radical. Alternatively, the charge can be retained on the olefin fragment (r) when a neutral mercaptan molecule is eliminated (II → r).



Some conclusion can be derived from the deuterium labeling results in the *n*-amyl isoamyl (Table V and Figure 3) and *n*-amyl isopropyl (Table IV and Figure 1) sulfides about the transition of C_5 fragments into C_4 allylic species. To the extent of 80%, the terminal methyl group is lost from the pentyl chain in forming the C_4 ion. A possible mechanism is given.



In summary, it may be stated that the presently described deuterium labeling results show a close resemblance between ethers and thioethers as far as the size of the transition state in the key hydrogen rearrangement step leading to species e and f is concerned, but at the same time they indicate that variations in the heteroatom may cause substantial differences—especially of a quantitative nature—in some of the characteristic fragmentation processes.

Experimental Section[15]

Isopropyl *n*-Butyl Sulfide (II) and Labeled Analogs VIII–XIII. Isopropyl mercaptan (0.1 ml) and *n*-butyl bromide (0.08 ml) were heated under reflux in 2 ml of 10% aqueous potassium hydroxide for 12 hr. The sulfide was extracted with ether and purified by gas chromatography on a 15% PDEAS column at 95°. The labeled d_2-butyl bromides were prepared by the earlier described procedures.[16] Perdeuterio-*n*-butyl bromide was prepared by lithium aluminum deuteride (0.430 g) reduction of perdeuteriobutyric acid (1g) (Merck Sharp and Dohme, Montreal) followed by conversion of the alcohol to the bromide with 4 ml of 48% hydrobromic acid and 1 ml of concentrated sulfuric acid. α-d_1-Isopropyl bromide was prepared by reduction of acetone (1 g) with lithium aluminum deuteride (0.25 g) in ether followed by conversion to the bromide with 4 ml of 48% hydrobromic acid and 1 ml of concentrated sulfuric acid. The same procedure was used in the synthesis of d_6-isopropyl bromide from d_6-acetone. These bromides were condensed with butyl mercaptan to form the desired sulfide.

Isopropyl *n*-Amyl Sulfide (I) and Labeled Analogs XIV–XIX. The sulfides were prepared in the same manner as described above with substitution of 100 mg of *n*-amyl bromide. The sulfides were purified by gas chromatography on a polybutylene glycol column at 100°. The labeled bromides were synthesized according to the earlier described procedure.[6a]

***n*-Amyl Isoamyl Sulfide (IV) and Labeled Analogs XX–XXVI.** Labeled *n*-amyl bromides[6a] were treated with isoamyl mercaptan in 10% aqueous potassium hydroxide to yield *n*-amyl isoamyl sulfides. These sulfides were purified by gas chromatography on a polybutylene glycol column at 100°. 1,1-d_2-Isoamyl bromide was synthesized by reduction of isovaleric acid (1 g) with lithium aluminum deuteride (0.410 g) in ether and subsequent conversion of the alcohol to the bromide by treatment at reflux with 4 ml of 48% hydrobromic acid and 1 ml of concentrated sulfuric acid. α-d_1-Isopropyl bromide (from 2 g of acetone) was converted to β-d_1-isovaleric acid by a malonic ester synthesis. This acid was reduced and the alcohol converted to the bromide as described above to form γ-d_1-isoamyl bromide. These isoamyl bromides were condensed with *n*-amyl mercaptan forming the desired *n*-amyl isoamyl sulfides.

Ethyl *n*-Hexyl Sulfide and Labeled Analog VI. These sulfides were prepared in the manner described earlier using ethyl mercaptan and hexyl bromide. The 4,4-d_2-*n*-hexyl bromide preparation has been described.[6a]

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(15) All mass spectra were measured with an Atlas CH-4 mass spectrometer equipped with an AN-4 ion source (temperature 60°) and a logarithmic transfer recorder.[12] The ionizing energy was maintained at 70 ev. We are indebted to Drs. R. T. Aplin and A. M. Duffield for the measurements and for advice in the numerous calculations. All sulfides were purified by gas phase chromatography using a Wilkens Aerograph instrument

(16) A. M. Duffield, R. Beugelmans, H. Budzikiewiicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 805 (1965).

4,4-d_2-n-Hexyl Mercaptan (VII). 4,4-d_2-Hexyl bromide[6a] (0.5 g) was dissolved in reagent grade acetone and added dropwise to a solution of 0.5 g of potassium ethyl xanthate in acetone. After stirring for 1 hr, the precipitated potassium bromide was filtered, and the product was extracted with chloroform. The xanthate was converted[17] to the mercaptan by heating under reflux with lithium aluminum hydride (0.5 g) in ether for 3 hr. The mercaptan was purified by gas chromatography on polybutylene glycol at 100°.

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(17) C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, *J. Am Chem. Soc.*, 77, 568 (1955).

Organic Polymers. Correlation between Their Structure and Catalytic Activity in Heterogeneous Systems.

II. Models for Dehydrogenation Catalysts

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Contribution from the Plastics Research Laboratory, Polymer Department, The Weizmann Institute of Science, Rehovoth, Israel. *Received November 24, 1965*

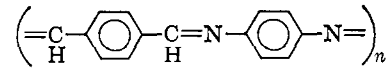
Abstract: The activity of two polymers as heterogeneous catalysts in dehydrogenation reactions in the vapor phase is described. While they have similar stuctures, one is active and the other is not. Both have an extended system of conjugated double bonds, but only the active one has quinoid rings. It is thus shown that it is the latter property that is required for catalytic activity in dehydrogenation. In addition, the concept is tested by using two thermostable organic compounds of known and almost identical structures as catalysts, where likewise the one containing a quinoid unit is active and the other is not. There seems to be a clear correlation between the concentration of free spins as measured by esr and activity toward dehydrogenation, but no correlation can be found with the semiconducting properties of the materials. The importance of these results, which show that the chemical units and not the electronic properties of the solid are responsible for catalytic activity, is discussed, and compared with current theories about the activity of inorganic catalysts.

In a previous publication[1] we reported the catalytic activity of pyrolyzed polyacrylonitrile and polycyanoacetylene in the dehydrogenation of cyclic olefins in the vapor phase. A mechanism was proposed which attributed this activity to conversion of the quinoid annularly condensed ring system of the catalyst into a hydroaromatic one. In the present publication we intend to prove this concept by describing the catalytic behavior of two poly-Schiff bases, very similar in structure and both containing a polyconjugated system of double bonds. One of them, being polyaromatic, cannot be stabilized by taking up hydrogen and is catalytically inactive. The other one is polyquinoid and is capable of dehydrogenating cyclic olefins in the same way as do pyrolyzed polyacrylonitrile and polycyanoacetylene. To demonstrate that the quinoid unit, and not the extended system of conjugated π electrons, is of overriding importance for the catalytic behavior, results are also given for dehydrogenation reactions over two thermostable organic compounds with a defined structure, which show the same dependence of catalytic behavior on structure.

All dehydrogenations described follow the same pattern in that hydrogen is transferred from the gaseous reactant to the solid, as a result of which the latter is gradually inactivated. A short treatment with air at 150° restores the activity entirely. If the reagent is passed together with air, no deactivation occurs. One may therefore regard this as catalytic activity and not as a reaction between a solid phase and a gaseous reactant only.

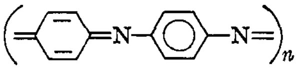
Catalysts

1. AA. Condensation Product of Terephthalaldehyde with p-Phenylenediamine. The structure assigned to this product is



and its thermal and electrical properties have been studied.[2,3] The structure sketched above is polyconjugated aromatic. Uptake of hydrogen would disturb the conjugation and is therefore energetically unfavorable. Consequently this polymer can be expected to be inactive as a dehydrogenation catalyst, as is confirmed by experiment.

2. KA. Condensation Product of Cyclohexanedione-1,4 with p-Phenylenediamine. A polymer of the structure



has been described in the literature.[4,5] It is commonly thought to be formed by the oxidation of aniline. Because of the uncertainty about the structure of aniline black,[6] however, we looked for an alternative synthesis.

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(3) A. V. Topchiev, V. V. Korshak, U. A. Popov, and L. D. Rosenstein, *J. Polymer Sci.*, C4, 1305 (1963).

(4) A. A. Berlin, *et al.*, *Dokl. Akad. Nauk SSSR*, **134**, 1123 (1960).

(5) H. A. Pohl and E. H. Engelhardt, *J. Phys. Chem.*, **66**, 2085 (1962).

(6) G. A. Swan and D. G. I. Felton, "The Chemistry of Heterocyclic Compounds," Vol. XI, Weissberger, Ed., Interscience Publishers Inc., New York, N. Y., 1957, p 165.