from that in benzene by changing two resonance integrals (β_{12} and β_{56} for example) by a relatively small amount, all quantities in the former molecule should be obtained from those in the latter by some simple perturbation calculation. Thus for the mobile bond orders we have *e.g.*[5]

$$(p_{34})_{\text{thiophene}} = (p_{34})_{\text{benzene}} + \left(\frac{\partial p_{34}}{\partial \beta_{12}}\right)_{\text{benzene}} \times \delta\beta_{12} + \left(\frac{\partial p_{34}}{\partial \beta_{56}}\right)_{\text{benzene}} \times \delta\beta_{56} \quad (4)$$

(numbering of thiophene: See section 4 of this paper; 1 and 6 refer to the conjugating sulfur hybrids.) The quantities $(\partial p_{rs}/\partial \beta_{tu})$ are written $\pi_{rs,tu}$ and called "*mutual bond polarizabilities.*" They may readily be calculated[14,20] for benzene and naphthalene. For benzene we find, for example[20]

$$\pi_{34,12} = \pi_{34,56} = 7/(54\beta)$$

In benzene all bond orders p_{rs} are 0.667. With $\delta\beta_{12} = \delta\beta_{56} = -(1/5)\beta$, (4) finally yields

$$(p_{34})_{\text{thiophene}} = 0.667 - \frac{2 \times 7}{5 \times 54} = 0.615$$

in good agreement with the direct calculation, which yielded 0.612 (see section 4 above). In Table II we have collected all mobile bond orders in thiophene and isothianaphthene, calculated (i) directly, (ii) by the perturbation method.

TABLE II

MOBILE BOND ORDERS IN THIOPHENE AND ISOTHIANAPHTHENE, CALCULATED DIRECTLY AND BY PERTURBATION METHOD

Numbering: See section 4 of this paper.

	Thiophene			Isothianaphthene	
	Direct	Perturbation		Direct	Perturbation
$p_{12} = p_{15}$	0.582	0.593	$p_{12} = p_{23}$	0.646	0.658
$p_{23} = p_{45}$	.727	.726	$p_{18} = p_{39}$	.608	.608
p_{34}	.612	.615	p_{89}	.489	.491
			$p_{78} = p_{49}$	.537	.538
			$p_{67} = p_{45}$	.736	.735
			p_{56}	.589	.590

In general the perturbation method yields satisfactory results, except for the C–S bonds which come out 0.010 to 0.012 too high. Unpublished calculations by L. R. Blue and the present author indicate a similar discrepancy in some other conjugated sulphur compounds. Thus the perturbation method would give free valencies for α-carbon atoms which are about 0.01 too low. Since we are interested in small differences in free valencies, such deviations are undesirable.

Our conclusion is that direct calculations should be given preference if not too much labor is involved. The perturbation method however leads to generally good results, in particular if an empirical correction of −0.01 is applied to the mobile bond orders of all C–S bonds.

BOULDER, COLORADO

[20] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A193**, 447 (1948).

[CONTRIBUTION NO. 3376 FROM DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH LABORATORIES]

The Thermal Decomposition of Mercaptans

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The thermal decompositions of benzyl, methyl and ethyl mercaptans have been investigated in a flow system in the presence of a large excess of toluene as a carrier gas and a free radical trap. Benzyl mercaptan decomposes by a homogeneous, first-order free radical process with an activation energy of 53(±2) kcal. mole^{-1}, which has been identified with the dissociation energy of the C–S bond. Methyl mercaptan also decomposes by a free radical mechanism but the process is more complicated. The activation energy, identified with the C–S bond dissociation energy, was calculated to be 67 kcal. mole^{-1} on the assumption of a constant frequency factor. Ethyl mercaptan decomposes principally by intermolecular rearrangement to C_2H_4 and H_2S and also by a split of the C–S bond to yield ethyl and hydrosulfide radicals. The molecular process appears to be somewhat heterogeneous with an activation energy that decreases from about 55 kcal. mole^{-1} to about 48 kcal. mole^{-1} with decreasing temperature. The activation energy for the free radical reaction, which is identified with the C–S bond dissociation energy, was calculated to be 63.5 kcal. mole^{-1} on the assumption of a constant frequency factor. From the above values of D(CH_3–SH) and D(C_2H_5–SH) together with relevant thermochemical data the heat of formation of the SH radical was estimated to be 32 and 31 kcal. mole^{-1}, in reasonable agreement with the value of 38.4 (±5.0) kcal. mole^{-1} derived by Franklin and Lumpkin from the appearance potentials of carbonium ions from various mercaptans.

Introduction

Although the properties of bonds between sulfur and carbon are of considerable theoretical and practical importance there is very little quantitative information available about the dissociation energies of such bonds or about the mechanisms and kinetics of the thermal decomposition of organic sulfur compounds. Thus there is disagreement about such fundamental quantities as the heat of formation of sulfur atoms and the dissociation energies of the bonds in H_2S.

Porter[2a] and Herzberg and Ramsay[2b] have estimated spectroscopically the S–H bond dissociation energy in the hydrosulfide radical to be about 85 kcal. mole^{-1}. Franklin and Lumpkin,[3] from the appearance potentials of carbonium ions from various mercaptans and relevant thermochemical data, have derived a value of 38.5 (±5) kcal. mole^{-1} for the heat of formation of the hydrosulfide radical. This may be shown[4] to lead to

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[1] (a) N.R.C. Post-Doctoral Fellow 1951–1952; Department of Experimental Medicine, McGill University, Montreal, P. Que.; (b) Olin Industries, Inc., New Haven, Connecticut.

[2] (a) G. Porter, *Disc. Faraday Soc.*, No. 9, 60 (1950); (b) G. Herzberg and D. A. Ramsay, *ibid.*, No. 9, 80 (1950).

[3] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **73**, 1023 (1952).

[4] (a) A. H. Sehon, *ibid.*, **74**, 4722 (1952); (b) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

dissociation energies of 90 to 95 kcal. mole^{-1} for D(H–SH) in H_2S and 80 to 85 kcal. mole^{-1} for D(S–H) in the hydrosulfide radical, in reasonable agreement with Porter and Herzberg and Ramsay.

The mechanisms of the thermal decompositions of organic sulfur compounds have been investigated spasmodically over the last twenty years or so and there appears to be serious disagreement between Malisoff and Marks[5] and Trenner and Taylor[6] on the mechanism of the decomposition of ethyl mercaptan. More recently Ball and his co-workers[7] have studied the pyrolyses of 2-methyl-2-propanethiol and 1-pentanethiol. The results of those experiments were not clear cut but it was concluded that the former substance decomposed by a free radical process and the latter by a direct molecular rearrangement.

We have adopted the technique developed by Szwarc,[8] of using a large excess of toluene as a carrier and a free radical trap, to simplify the nature of the reaction in the hope that this would permit more definite information to be obtained about the mechanism and so allow the bond dissociation energies to be measured.

Experimental

The materials used in these experiments were the purest samples available commercially and were further purified by distillation *in vacuo*. The benzyl and ethyl mercaptans were obtained from the Eastman Kodak Company; the methyl mercaptan from the Mathieson Company; the toluene was the Phillips Petroleum Company's Research Grade Product. Blank experiments showed this grade of toluene to be sufficiently pure for our purposes. Deuterated benzyl mercaptan ($C_6H_5CH_2SD$) was prepared by neutralizing $C_6H_5CH_2SNa$ with D_2SO_4 followed by distillation to remove water and other impurities.[9]

The reaction vessel was constructed of quartz, the main portion being 20.5 cm. long and 3.8 cm. inside diameter. A quartz thermocouple well, 1.3 cm. outside diameter, extended from the inlet end through the reaction vessel proper and terminated about 7 cm. beyond the exit end of the effective reaction volume. A second vessel, essentially identical with the first, was packed with fine quartz fibers of uniform diameter of 4 × 10^{-2} mm.[10] The effective volumes and surface areas of these vessels were as follows

Vessel	Volume, cm.^{3}	Surface, cm.^{2}	S/V, cm.$^{-1}$
I	198	328	1.65
II (packed)	193	5408	28.02

The reaction vessel was enclosed in a well-insulated furnace whose outside dimensions were 18″ × 18″ × 36″. The furnace was wound in five sections to enable the temperature differential across the vessel to be minimized, the temperature distribution over the length of the effective reaction volume being within ±0.5°. The tubing which connected the reaction vessel to the inlet and exit capillaries was heated to prevent condensation. The working pressures and flow rates were controlled by altering the dimensions of those capillaries.

The mercaptans were introduced through a fine capillary into an excess of toluene vapor and the mixture flowed through a heated tube to the reaction vessel. The condensable products of the reaction, together with undecomposed toluene and mercaptan, were removed in traps maintained at 0, −80 and −195°, respectively. The uncondensable products were pumped by means of a mercury diffusion pump into a calibrated volume.

At the end of the experiment the pressures of the uncondensable gases were measured (McLeod gage) and a sample analyzed by combustion over copper oxide or mass spectrometrically.[11] In all cases the uncondensable gas consisted entirely of hydrogen and methane.

In the experiments with deuterated benzyl mercaptan the isotopic nature of the uncondensable gas was established by mass spectrometric analysis. No D_2 was found and only small percentages of HD were present, even at the highest temperatures used.

Since toluene itself decomposes slightly under some of the conditions pertaining in these experiments, blank experiments were done with toluene alone and the rate of production of H_2 and CH_4 corrected accordingly. These blank corrections amounted to not more than 25% of the total uncondensable gases produced under the most drastic conditions.

The dibenzyl formed in the experiments with benzyl mercaptan was trapped at 0° and the undecomposed toluene condensed at −60°. Due to the very low volatility of benzyl mercaptan compared to H_2S their separation was readily achieved by condensing them in traps at −60° and −195°, respectively. The H_2S was then absorbed by sodium hydroxide solution and titrated iodometrically after acidification with HCl.

This method of separating H_2S from the undecomposed mercaptan was not used in the experiments with methyl and ethyl mercaptan because of the proximity of the boiling points. In these cases both H_2S and the mercaptan were absorbed in 2 *N* $AgNO_3$. The combined precipitates of silver sulfide and mercaptide were filtered and the number of silver ions precipitated calculated by titration of the filtrate.[12] Since there are two replaceable protons in H_2S and only one in mercaptans, the number of moles of mercaptan decomposed is equal to the number of moles of silver ions removed by precipitation less the number of moles of mercaptan passed through the reaction vessel. When a large percentage of the mercaptan is decomposed this method gives fairly accurate results but when the decomposition is small its extent is measured as the small difference between two large quantities. Under those conditions the determination may be rather inaccurate because of handling losses, even though the two quantities can be measured quite precisely.

The bibenzyl was produced as a white crystalline solid which melted at 49–52°. However, the ultraviolet spectrum showed the presence of from 2 to 10% of stilbene.[13]

Results

Benzyl Mercaptan.—The products of the decomposition of benzyl mercaptan in excess of toluene were principally hydrogen sulfide and bibenzyl, in approximately equal quantities, with smaller amounts of uncondensable gas consisting of H_2 (65 to 75%) and CH_4 (25 to 35%). The results (Table I) show that the ratio of bibenzyl to H_2S was approximately unity and was not affected by changes in the surface to volume ratio or by temperature. The hydrogen and methane together were about 20% of the H_2S formed and again, this ratio was independent of packing and of the temperature.

The effect of changing various parameters such as temperature, pressures of benzyl mercaptan and toluene, contact time, and surface to volume ratio on the rate of decomposition is shown by the data in Table II and graphically in Fig. 1. The percentage decomposition was calculated on the assumption that a molecule of H_2S was formed for

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(5) W. M. Malisoff and E. M. Marks, *Ind. Eng. Chem.*, **23**, 1114 (1931); *J. Chem. Phys.*, **1**, 284 (1933).

(6) N. R. Trenner and H. A. Taylor, *ibid.*, **1**, 77 (1933).

(7) C. J. Thompson, R. A. Meyer and J. S. Ball, THIS JOURNAL, **74**, 3284, 3287 (1952).

(8) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948); **17**, 431 (1949).

(9) We are indebted to Dr. L. C. Leitch and Mr. A. T. Morse of the Applied Chemistry Division for this preparation.

(10) We are indebted to Mr. C. H. Bayley of the Textile Laboratories for these measurements.

(11) We are indebted to Dr. F. Lossing for the mass spectrometric results.

(12) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1940, p. 291.

(13) We are indebted to Dr. C. Sandorfy for the spectrum.

TABLE I

PYROLYSIS OF BENZYL MERCAPTAN—PRODUCTS OF THE REACTION

Expt.[a] no.	Temp., °K.	Dibenzyl / H_2S	$H_2 + CH_4$ / H_2S
6	760	0.94	0.10
13	816	.89	.19
19	830	.83	.21
16	831	1.04	.17
5	834	0.98	.25
32-P.D	836	1.06	.15
10	849	0.97	.22
9	877	.96	..
21	878	.97	.19
22	879	1.06	.16
29-P	976	0.95	..
33-P	1020	0.99	..

[a] "P" denotes experiments with a packed reaction vessel and "D" those with $C_6H_5CH_2SD$.

each molecule of the mercaptan decomposed and the rate constant on the assumption that the process was first order. It is seen (Fig. 1) that the Arrhenius plot gives a reasonably straight line and that *k* was not significantly affected by changes in pressure, contact time or surface to volume ratio. This is considered additional support for the first-order character and the homogeneity of the thermal decomposition of benzyl mercaptan. The slope of the Arrhenius line corresponds to an activation energy of 53 kcal. mole^{-1}.

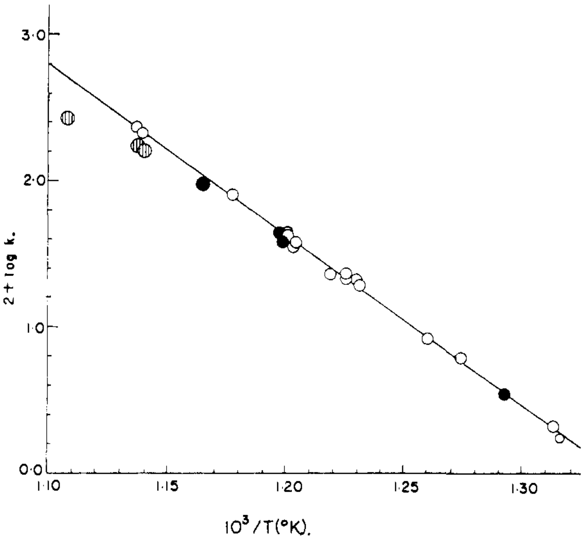

Fig. 1.—The thermal decomposition of benzyl mercaptan—Arrhenius plot: filled points denote experiments in the packed vessel; shaded points denote experiments in which more than 60% of the benzyl mercaptan was decomposed.

Discussion

The results have shown that the decomposition of benzyl mercaptan is predominantly homogeneous and first order and that H_2S and bibenzyl, the principal products of the reaction, are formed at equal rates. These observations are most readily explained by the series of reactions

$$C_6H_5{\cdot}CH_2{\cdot}SH \longrightarrow C_6H_5{\cdot}CH_2{\cdot} + {\cdot}SH \quad (1)$$

$$SH + C_6H_5{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}CH_2{\cdot} + H_2S \quad (2)$$

$$2C_6H_5{\cdot}CH_2{\cdot} \longrightarrow C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5 \quad (3)$$

TABLE II

THE THERMAL DECOMPOSITION OF BENZYL MERCAPTAN EFFECT OF CONDITIONS ON THE RATE

Expt.[a] no.	Temp., °K.	$P_{tot.}$, mm.	P_{RSH} × 10², mm.	τ, sec.	Dec., %	k × 10², sec.$^{-1}$
6	760	11.7	13	0.76	1.28	1.7
11	761	12.0	13	.81	1.75	2.2
27(P)	774	12.2	14	.79	2.74	3.5
12	785	11.1	12	.72	4.5	6.4
7	793.5	10.4	13	.76	5.9	8.0
23	812.5	11.6	21	.97	17.4	19.7
15	813	12.2	65	.73	14.8	22.0
13	816	12.1	14	.75	16.2	23.5
14	816	12.2	29	.75	15.35	22.0
20	820	10.3	10	.34	7.6	23.3
19	830	19.4	35	.68	22.9	38.4
16	831	12.0	6.5	.74	24.0	37.0
17	832	5.7	16	.91	29.0	37.8
18	832	20.2	147	.65	24.4	42.7
25(P)	833	11.8	11	.72	24.6	39.2
5	834	11.2	13	.66	25.0	43.5
D-32(P)	836	11.8	14	.70	25.4	41.6
10	849	10.9	12	.64	40.3	81.0
24(P)	859	12.3	12	.70	48.8	95.5
21	878	10.7	15	.32	49.0	213
22	879	10.7	7	.31	50.2	228
9	877	11.86	13	.68	67.2	164
3	878	12.50	9	.645	67.3	173
8	903	11.59	11	.66	83.3	272

[a] P denotes experiments in the packed vessel. D denotes experiments with deuterized benzyl mercaptan.

This scheme is entirely analogous to the type of mechanism suggested by Szwarc[8] to account for the thermal decomposition of a number of similar benzyl derivatives in the presence of toluene. Either of the alternative initial reactions

$$C_6H_5{\cdot}CH_2{\cdot}SH \longrightarrow C_6H_5CH_3 + S \quad (1')$$

$$\text{or} \longrightarrow C_6H_5CH\colon + H_2S \quad (1'')$$

would be equally satisfactory kinetically, provided that sulfur atoms or $C_6H_5{\cdot}CH\colon$ radicals are capable of abstracting hydrogen from toluene. However, it would be difficult to reconcile either of these reactions with some of Szwarc's results, for example the agreement between the heats of formation of NH_2 radicals derived from the decomposition of hydrazine[14] and benzylamine[15] in the presence of toluene. Hence, in the absence of contrary evidence, we may assume that reactions 1, 2 and 3 represent the mechanisms by which the principal products are formed.

However, this mechanism does not explain the fact that hydrogen and methane are produced, even though in minor quantities, in addition to H_2S and bibenzyl. It should be noted here that hydrogen and methane were also formed when benzyl bromide[16] was decomposed under similar conditions. It was then suggested that the radicals reacted with bibenzyl to abstract hydrogen

$$R + C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CH{\cdot}CH_2{\cdot}C_6H_5 + RH \quad (4)$$

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(14) M. Szwarc, *Proc. Roy. Soc.* (*London*), **A198**, 267 (1949).

(15) M. Szwarc, *ibid.*, **A198**, 285 (1949).

(16) M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

and that the radical so formed decomposed

$$C_6H_5{\cdot}CH{\cdot}CH_2{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + H \quad (5)$$

to yield stilbene and a hydrogen atom. Szwarc[8] has suggested that H atoms react with toluene to produce either H_2 and a benzyl radical

$$H + C_6H_5{\cdot}CH_3 \longrightarrow C_6H_5CH_2{\cdot} + H_2 \quad (6)$$

or benzene and a methyl radical

$$H + C_6H_5{\cdot}CH_3 \longrightarrow C_6H_6 + CH_3{\cdot} \quad (7)$$

and that the methyl radical abstracts hydrogen from another molecule of toluene to yield methane and a benzyl radical. Horrex and Miles[16a] have recently suggested that even benzyl radicals are capable of reacting in reaction 4, so that, in the present reaction, R may be either a benzyl or a hydrosulfide radical. This suggestion receives support from the fact that, in some of our experiments, as much as 10% of stilbene was observed in the "bibenzyl."

The results of experiments with deuterated benzyl mercaptan provide some information about the stability of hydrosulfide radicals. The absence of D_2 and the very small amount of HD in the uncondensable products (*i.e.*, 1.5% of the H_2S produced at 870° K.) show that, under the conditions of these experiments, the hydrosulfide radical is stable, in agreement with the results obtained from the photochemical decomposition of hydrogen sulfide at high temperatures.[17] The absence of D_2 also shows that the hydrosulfide radicals reacted much more rapidly with toluene, reaction 2, than by the process

$$2HS \longrightarrow H_2 + S_2$$

which has been suggested[17] to occur under different conditions. To extend further this investigation of the stability of hydrosulfide radicals, experiments with deuterated benzyl mercaptan were done at temperatures as high as 1020° K. and with contact times of about 0.6 sec. No D_2 was found and the HD produced amounted to not more than 3% of the H_2S. Hence it may be concluded that the SH radicals do not decompose to a significant extent even under such drastic conditions. These results lend added support to our assumption that the rate of decomposition of benzyl mercaptan is adequately measured by the rate of formation of H_2S.

The results shown in Fig. 1 appear to indicate that the Arrhenius plot is not really a straight line since the rate constant in some experiments at high temperatures is lower than expected. Thus the values of k are significantly lower in experiments numbers 9 and 13, at 877 and 878° K. with 67.2 and 67.3% conversion, respectively, than would be expected from the results at the lower temperatures (Table II). However, in experiments 21 and 22, at almost the same temperatures but with lower contact times and, consequently, lower percentage decompositions (49.0 and 50.2%), the values of k are in excellent agreement with those predicted. Since at lower temperatures the value of k is independent of contact time, we do not consider that the above mentioned effect was caused by the change in contact time *per se*, but to the excessive extent of decomposition, leading to a significantly higher concentration of H_2S or of SH radicals. The high concentration of H_2S might favor the occurrence of the reaction

$$R + H_2S \longrightarrow RH + HS{\cdot}$$

and the high concentration of HS radicals might lead to the recombination reactions

$$C_6H_5{\cdot}CH_2{\cdot} + {\cdot}SH \longrightarrow C_6H_5{\cdot}CH_2{\cdot}SH$$

or

$$2SH \longrightarrow H_2S_2$$

outside the reaction volume proper, and thus to an abnormally low apparent percentage decomposition. Therefore, the fact that the point on the Arrhenius plot for experiment number 8 at 903° K. and with 83.3% decomposition, fell significantly below the line is not considered indicative of complications in the kinetics.

If the foregoing analysis is correct and if the recombination of hydrosulfide and benzyl radicals (reverse of reaction 1) proceeds with zero activation energy, then the activation energy observed for reaction 1 will be identical with the C–S bond dissociation energy in benzyl mercaptan. Our results indicate that this value is 53 (± 2) kcal. $mole^{-1}$ and that the frequency factor of the decomposition is, within a factor of about 3, equal to 3×10^{13} $sec.^{-1}$. Since the heat of formation of benzyl mercaptan is not known it is not possible to derive from these data the heat of formation of hydrosulfide radicals. Some indication of that quantity was obtained from the experiments with methyl and ethyl mercaptans.

Methyl and Ethyl Mercaptans.—The thermal decompositions of methyl and ethyl mercaptans were investigated between 1005 to 1102°K. and from 785 to 938°K., respectively; the conditions and results of the experiments are presented in Tables III and IV. These investigations were not as thorough as those on benzyl mercaptan, since the effect of contact time was not investigated and the effects of surface to volume ratio and pressure were investigated only with methyl mercaptan,

TABLE III

THE THERMAL DECOMPOSITION OF METHYL MERCAPTAN

EFFECT OF TEMPERATURE ON THE RATE

Expt.[a] no.	Temp., °K.	P_{total}, mm.	P_{CH_3SH}, mm.	τ, sec.	Dec., %	$10 \times k_1$, $sec.^{-1}$	E,[a] kcal./mole
2(P)	1005	12.7	0.37	0.61	9.4	1.4	66.3
1(P)	1015	12.7	.36	.55	12.5	2.4	65.8
13	1022	25.3	.48	.53	9.1	1.8	67.0
12	1024	6.0	.66	.69	23.7	3.9	65.5
11	1024 5	12.5	.57	.60	21.4	4.0	65.5
4(P)	1059.5	7.0	.31	.67	10.2	1.6	69.5
5(P)	1059.5	12.5	.42	.57	25.0	4.6	67.3
6(P)	1059.5	25.4	.71	.50	44.7	11.8	65.4
7	1065	12.6	.55	.59	29.3	5.9	67.3
8	1056.5	12.2	.21	.58	30.8	6.3	67.1
9	1066	6.0	.20	.68	20.7	3.4	68.4
10	1066	24.5	.50	.53	41.4	10.1	66.1
3(P)	1102	12.7	.44	.53	40.0	9.5	68.5

[a] E was calculated by assuming a frequency factor of 3×10^{13} $sec.^{-1}$.

[16a] C. Horrex and S. E. Miles, *Disc. Faraday Soc.*, **10**, 187 (1951).

[17] B. deB. Darwent and R. Roberts, *Proc. Roy. Soc.* (*London*) **A216**, 344 (1953).

Table IV

The Thermal Decomposition of Ethyl Mercaptan

Expt. no.	Temp., °K.	P_{total}, mm.	$P_{C_2H_5SH}$, mm.	τ, sec.	$k_a \times 10$, sec.$^{-1}$	E_a[a]	$k_b \times 10^2$ (sec.$^{-1}$)	E_b[a]
5	785	13.3	0.68	0.83	3.4	48.5	...	..
1	787	20.0	.66	.78	4.9	48.0	...	..
4	868	12.5	.60	.69	4.9	53.5	0.39	63.5
3	891	12.4	.61	.68	6.1	54	1.5	63
2	916	13.5	.62	.60	9.2	55	2.3	63.5
6	917	13.2	.74	.64	9.7	55	4.4	62.5
7	938	12.9	.61	.49	18.1	55	14.9	62

[a] Subscripts a and b refer to the molecular and free radical process, respectively. The activation energies were calculated from assumed frequency factors.

but they do provide some information about the mechanisms of the reactions and the bond dissociation energies involved.

The only products identified in the decomposition of methyl mercaptan were methane, H_2S, hydrogen and bibenzyl. The uncondensable gases contained between 71 and 95% methane and this composition appeared to be independent of temperature, pressure and surface to volume ratio. The ratio of bibenzyl to H_2S varied irregularly between 0.46 and 0.80. Large corrections for the decomposition of toluene were necessary with methyl mercaptan and, at the highest temperature, the uncondensable gases from toluene amounted to 85% of the total. The correction was made by simple subtraction on the assumption that the decomposition of toluene did not in itself influence the decomposition of the mercaptan. The products from ethyl mercaptan at low temperatures consisted entirely of H_2S and C_2H_4. No bibenzyl was produced. At high temperatures H_2S and C_2H_4 were still the major products but hydrogen, methane and bibenzyl also were produced, their importance increasing with increasing temperature.

Although the decompositions were found to be rather erratic the results are not inconsistent with the suggestion that methyl mercaptan decomposes by a free radical process

$$CH_3SH \longrightarrow CH_3\cdot + SH\cdot \qquad (8)$$

and ethyl mercaptan by two separate processes, the decomposition being a molecular rearrangement

$$C_2H_5SH \longrightarrow C_2H_4 + H_2S \qquad (9)$$

at low temperatures and a free radical decomposition

$$C_2H_5SH \longrightarrow C_2H_5 + SH \qquad (10)$$

which becomes of increasing importance at high temperatures. Over the whole of the temperature range studied, the molecular rearrangement was by far more important.

The rates of the reactions were calculated on the assumptions that the rate of decomposition of methyl mercaptan was equal to the rate of production of H_2S, that the rate of the free radical decomposition of ethyl mercaptan was equal to the rates of production of $(H_2 + CH_4)$ and that the rate of the molecular decomposition of ethyl mercaptan was equal to the difference between the rate of production of H_2S and the sum of the rate of production of hydrogen and methane. The first-order rate constant for the decomposition of CH_3SH appears to be a function of the total pressure. This is reminiscent of the decomposition of methyl bromide[18] and may be caused by a falling off in the rate of energy transfer at low pressures as suggested[18] or it may indicate that methyl mercaptan reacts with toluene in a second-order process, for example

$$CH_3SH + C_6H_5CH_3 \longrightarrow C_6H_5CH_2CH_3 + H_2S$$
$$\text{or } C_6H_5CH_2 + CH_3 + H_2S$$

The mechanism of the decomposition of ethyl mercaptan appears to be heterogeneous at low temperatures and to approach a homogeneous process at higher temperatures.

Because of the complications in these reactions and the poor reproducibility of our measurements, we have not attempted a rigorous evaluation of the bond dissociation energies by the usual method of Arrhenius. Instead we have calculated the E's from the measured k's by assuming frequency factors of 3×10^{13} and 1×10^{13} sec.$^{-1}$ for the free radical decompositions and the molecular rearrangement, respectively; the activation energies so derived are given in Tables III and IV. It is obvious that this procedure may be far from sound but we find that the activation energies calculated in this way do not vary significantly with temperature or surface to volume ratio and that the dependence of E for methyl mercaptan on pressure is not very large. If we assume that the average "activation energies" (67 and 63 kcal. mole^{-1}) are equivalent to the C–S dissociation energies in methyl and ethyl mercaptans, respectively, then, by using the values[19] of -3.7 and -9.7 for the heats of formation of methyl and ethyl mercaptans and[20] 31 and 22 kcal. mole^{-1} for the heats of formation of methyl and ethyl radicals respectively, we calculate values of 32 and 31 kcal. mole^{-1} for the heat of formation of HS radicals. These values are in reasonable agreement with the value of 38.4 ± 5 kcal. mole^{-1} derived by Franklin and Lumpkin[3] for the heats of formation of SH radicals.

The results obtained from benzyl mercaptan were not as ambiguous as those from methyl and ethyl mercaptans. Those results should lead to a more firmly established value for the heat of formation of HS radicals when the heat of formation of benzyl mercaptan has been measured.

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