

The effect of this reversal is shown graphically in Fig. 3, where the elemental sulfur is seen to decrease between experiments at 25 and 30 seconds residence time. Butane/butene ratio measurements show a decrease of butane in this region. The resultant effect of reaction (2) gives a maximum in the curve for the formation of elemental sulfur shown in Fig. 6. This is an effect seen only in a relatively narrow temperature range as experiments at 375 and 425° showed almost no deviation from a smooth curve. Reaction (2) occurs to a very small extent at lower temperatures because of the low concentration of elemental sulfur. At the higher temperatures, the reverse reaction appears to be very rapid.

The reaction (3) of isobutene with elemental sulfur to give residual sulfur appears to follow closely the production of elemental sulfur. The product is probably a polysulfide material judging from the sulfur content.

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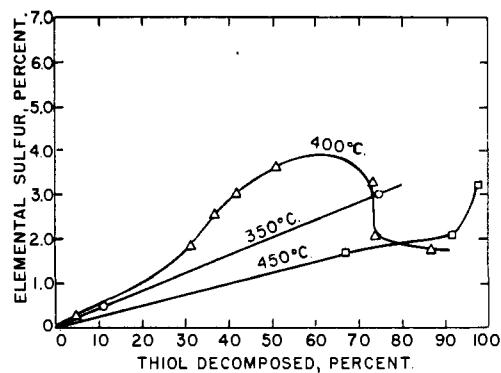


Fig. 6.—Elemental sulfur resulting from thiol decomposition at temperatures of 350, 400 and 450°.

the University of Wyoming. The authors wish to express their appreciation to the American Petroleum Institute, Research Project 48A, for the sample of 2-methyl-2-propanethiol used in this investigation.

LARAMIE, WYOMING

[CONTRIBUTION FROM THE BUREAU OF MINES, PETROLEUM AND OIL-SHALE EXPERIMENTAL STATION]

Thermal Decomposition of Sulfur Compounds. II. 1-Pentanethiol

By C. J. THOMPSON, R. A. MEYER AND J. S. BALL¹

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1-Pentanethiol was thermally decomposed in a quartz tube utilizing a flow method. The apparatus and techniques used in this investigation have been described in a previous publication. The conditions (350–500° with exposure times of 10 to 120 seconds) employed in this study resulted in decompositions ranging from 0.2 to 87%. The predominant sulfur-containing decomposition product was hydrogen sulfide. Small amounts of sulfides and residual sulfur were also produced. The decomposition, as postulated, proceeds by way of an intramolecular splitting of 1-pentanethiol to produce pentene and hydrogen sulfide.

Following the technique used by the authors² in their thermal decomposition studies on 2-methyl-2-propanethiol, 1-pentanethiol was decomposed under various conditions of time and temperature. The conditions employed in this study resulted in decompositions ranging from 0.2 to 87%. Satisfactory sulfur balances were obtained, and results were found to be reproducible. The predominant sulfur-containing decomposition product was hydrogen sulfide. Small amounts of sulfides and residual sulfur (compounds unreactive to ordinary reagents) were also produced. In addition, pentenes, butenes and other light hydrocarbons were found. Equations indicating some of the possible reactions involved in the decomposition are presented.

Apparatus and Procedure

Materials.—The 1-pentanethiol used in this investigation was 99.90 mole per cent. pure, as determined by the freezing-point method of Rossini.³ All other reagents were C. P. grade or better.

Apparatus.—The decompositions were made in a 25-mm. o.d. quartz combustion tube heated by a modified three-unit Hevi Duty organic combustion furnace. Furnace modifications included removal of the 1/2" transite end plates in all cases where two units came together, sealing of all

cracks between the upper and lower furnace sections with insulating cement, and the covering of the entire furnace with an asbestos blanket, 3 mm. in thickness. Except for these modifications, the furnace and feed mechanisms were the same in a previous investigation.² A heated inlet system (Fig. 1) containing a loose glass-wool plug in the lower end, was used to volatilize the 1-pentanethiol before its entry into the decomposition tube. This preheating eliminated rapid volatilization of the sample within the reaction tube, thereby minimizing undesirable surge. A U-shaped tube containing 15 ml. of isoöctane was attached to the lower end of the decomposition tube. A glass-wool gas-diffusion plug was held in the bottom of the outlet arm of the U-tube by means of several indentations in the tube. Exit gases from the U-tube were passed through a slant-tube gas scrubber containing 100 ml. of 33% sodium hydroxide. Low-boiling hydrocarbons in the exit gases from the scrubber were condensed in a trap cooled with a mixture of Dry Ice, carbon tetrachloride and chloroform.

Procedure. (a) **Temperature and Residence-Time Calibrations.**—These calibrations were made by the methods used in a previous investigation.²

(b) **Decomposition Procedure.**—After proper calibrations for temperature and residence time had been made, the reaction tube, U-tube, scrubber and cold trap were cleaned, reassembled and swept with nitrogen for 5 minutes. A hypodermic syringe containing 5 to 10 ml. of 1-pentanethiol was carefully weighed on an analytical balance and placed in the feed mechanism. The sample was fed into the furnace at the predetermined rate and the hypodermic syringe reweighed to determine the exact weight of sample added. The entire system was then swept with nitrogen for 10 minutes.

Analysis of Products (a).—Decomposition products remaining in the reaction tube and the liquid in the U-tube were composited and diluted to an accurate volume with

(1) To whom inquiries regarding this article should be sent.

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

(3) F. D. Rossini, *Anal. Chem.*, **20**, 110 (1948).

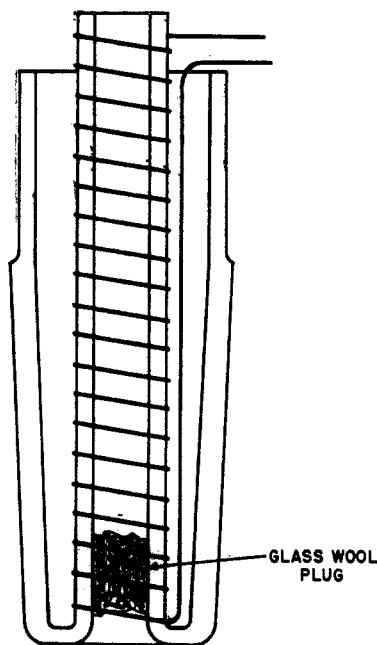


Fig. 1.—Heated inlet.

sulfur-free isoöctane. Suitable aliquots of this solution were then analyzed for total sulfur by the lamp method. Group sulfur analyses were carried out on other aliquots by the method of Ball.⁴

(b).—The liquid in the slant-tube gas scrubber was diluted to 500 ml. and a suitable aliquot taken for potentiometric determination of hydrogen sulfide and thiol. The method used was that of Tamele, Ryland and Irvine,⁵ modified to include hydrogen sulfide determination. Potentials were measured with a Beckman Laboratory Model pH meter.

(c).—The low-temperature condensed material was analyzed in a Consolidated Model 21-102 Mass Spectrometer.

Results and Discussion

Table I presents analytical data showing the effect of variation in time and temperature on the decomposition of 1-pentanethiol. These data were obtained by the decomposition of the pure sulfur compound in a quartz tube. These conditions simplify the problem by eliminating reactions with other compounds and by minimizing catalytic effects.

The reproducibility of the work can be observed by comparing, in Table I, duplicate runs made at the same temperatures and residence times. In Fig. 2, product composition is plotted against residence time. This treatment graphically depicts the simplicity of the reaction. The sum of undecomposed thiol and hydrogen sulfide represents more than 97% of the sulfur. There was no evidence of formation of tars or other high-molecular-weight material under any of the conditions employed in this investigation.

In Fig. 3, % thiol decomposed is plotted against residence time. The values recorded on the graphs were obtained from the data in Table I after prorating the loss.

The following reactions appear to be those involved in the decomposition

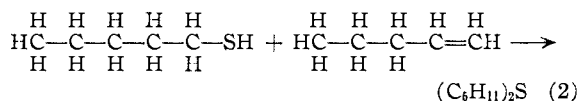
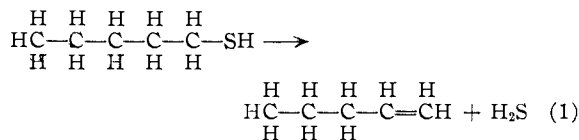
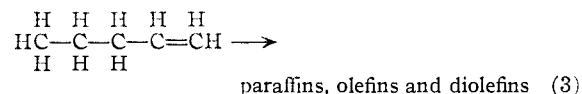


TABLE I

SUMMARY OF DECOMPOSITION EXPERIMENTS ON 1-PENTANETHIOL

Temp., °C.	Feed rate, g./min.	Residence time, seconds	Per cent. sulfur recovered as,					Residual sulfur	Sulfur recovery, %
			H ₂ S	RSH	Sulfides I ^a	Sulfides II ^b			
350	0.30188	30.00	0.2	98.1	0.0	0.0	0.0	98.3	
350	.12566	60.00	.2	98.1	.0	.0	.0	98.3	
350	.12868	58.59	.3	99.5	.0	.0	.0	99.8	
350	.08690	90.00	.4	94.2	.0	.0	.0	94.6	
350	.06681	120.00	.5	96.1	.6	.0	.6	97.8	
393	.26609	30.00	2.8	94.5	.0	1.4	.0	98.7	
393	.12163	60.00	3.4	92.3	.0	0.0	.7	96.4	
393	.12234	59.65	4.1	92.8	.0	0.7	.0	97.6	
393	.07353	90.00	4.7	93.5	.0	1.5	.0	99.7	
393	.05242	120.00	6.3	90.3	.7	0.7	.0	98.0	
450	.99204	10.00	6.8	89.8	.6	.6	.0	97.8	
450	.27362	30.00	17.1	77.1	.7	.7	.0	95.6	
450	.27308	30.06	16.6	78.4	.7	.7	.7	97.1	
450	.10742	60.00	30.5	63.6	1.4	.5	.5	96.5	
450	.05726	90.00	42.1	51.9	0.0	.3	.0	94.3	
500	.87802	10.00	38.0	57.2	0.5	.0	.5	96.2	
500	.19306	30.00	69.5	23.3	1.8	.2	.7	95.5	
500	.18858	30.28	69.7	22.5	2.0	.3	.3	94.8	
500	.08690	60.00	76.1	16.3	1.4	.5	.3	94.6	
500	.04740	90.00	80.3	12.1	1.4	.7	.2	94.7	

^a Material reactive with mercurous nitrate; probably aliphatic sulfides. ^b Material reactive with mercuric nitrate; probably aromatic sulfides or thiophenes



In reaction (1) the thiol is decomposed into pentene and hydrogen sulfide. This intramolecular splitting of 1-pentanethiol is in sharp contrast to the free radical mechanism proposed in the decomposition of 2-methyl-2-propanethiol.² Both the decomposition products and mass-spectrometer decomposition patterns suggest the molecular loss of hydrogen sulfide from the thiol molecule. In the mass spectrometer pattern of 1-pentanethiol, Fig. 4, the parent peak less 34 is at least 11 times that of the parent peak less 33 or 35 indicating removal of H₂S rather than SH or H₂S. The simultaneous breaking of the carbon-sulfur bond and a carbon-hydrogen bond and the almost instantaneous recombination of the two fragments is expected to contribute little, if any, to the reaction. However, a plausible explanation lies in the characteristics of the sulfur atom and the configuration of the thiol molecule. It is suggested that sulfur with its two pairs of available electrons has a definite affinity for a proton or protons from the adjacent carbon atom. At any given time the hydrogen or hydrogens on the carbon adjacent to the sulfur are sufficiently close to the sulfur atom as to lie within its sphere of influence so that the breaking of the carbon-sulfur bond results in the sulfur atom carrying with it one

(4) J. S. Ball, Bur. Mines Rept. Investigations, 3591 (1941).

(5) M. W. Tamele, L. B. Ryland and V. C. Irvine, *Ind. Eng. Chem., Anal. Ed.*, **13**, 618 (1941).

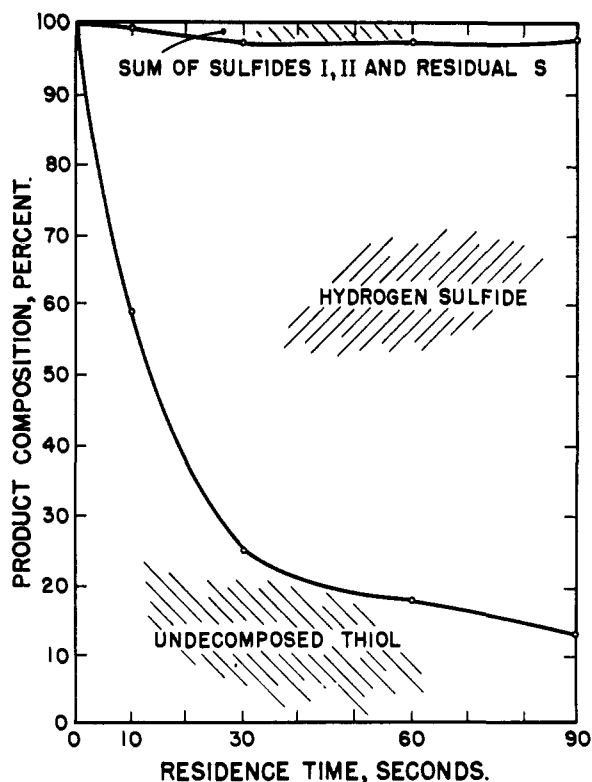


Fig. 2.—Effect of residence time on sulfur distribution at 500°.

or more hydrogens. The structure of the thiol determines the number of hydrogen atoms attracted to and removed with the sulfur. The structure of the 1-pentanethiol molecule favors the loss of hydrogen sulfide while in the case of 2-methyl-2-propanethiol the absence of hydrogens on the carbon atom adjacent to the sulfur dictates the loss of only an SH.

Additional evidence favoring this mechanism over a free radical mechanism is apparent from an examination of the type and quantity of decomposition products. The detection of only trace amounts of residual sulfur and tarry material and the complete absence of elemental sulfur support the proposed mechanism.

The decomposition data have been analyzed for order of reaction by the usual methods. Based on this treatment, it may be concluded that the reaction is in fair agreement with the requirements for a first-order reaction.

The small quantity of sulfides I reported in the table is probably produced as indicated in reaction (2). The small amount of material classified as sulfides II is produced from the reaction of hydrogen sulfide with the diolefins formed in reaction (3).

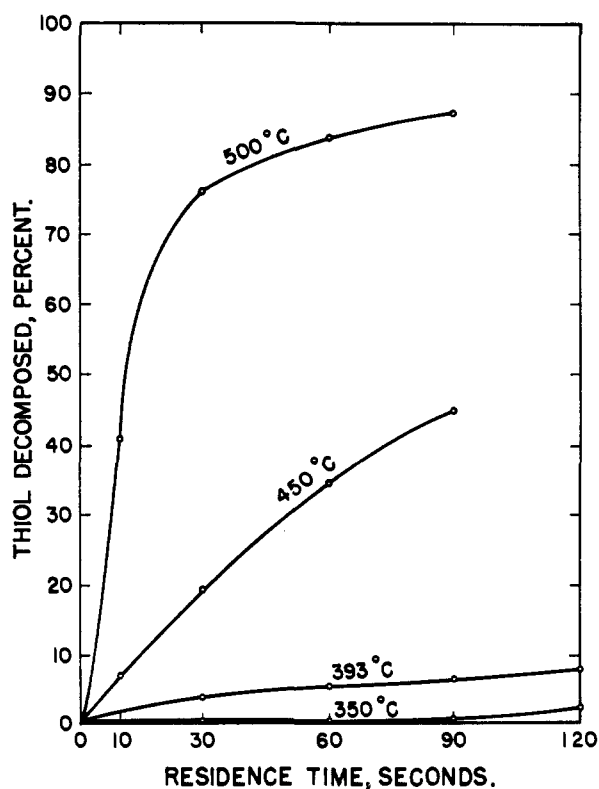


Fig. 3.—Thiol decomposed in relation to residence time at temperatures of 350, 393, 450 and 500°.

Mass spectrometer analyses of the low-boiling hydrocarbons produced by reactions (1) and (3) showed pentene to be the predominant product. However, at the higher temperatures the presence of such compounds as C₁-, C₂-, C₃-, C₄- and C₆-paraffins, the C₂-, C₃- and C₄-olefins and the C₄- and C₅-diolefins was detected.

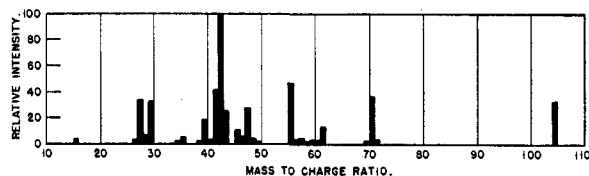


Fig. 4.—Mass spectra of 1-pentanethiol.

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LARAMIE, WYOMING