total volume changes for the reactions are tabulated, the time shown is the duration of illumination until the incremental volume change was less than 1% in a half hour. The only generalization which perhaps may be made is that the higher the ratio of phosphine to unsaturate, the faster the addition reaction takes place.

In Table II the reactant proportions for the various preparations and the products obtained together with the elemental analyses are summarized. The experiments with isobutene and allyl chloride are not included as no analytical data were obtained with the products of addition but only with the oxidation products. The figures given for the yields of the various products should be construed as indicating the order of the yields since handling losses were quite variable. The yield of 3-chloropropylphosphine was low even though the conversion of phosphine was 55%, as the main prod-

uct was a hard insoluble phosphorus-containing polymer.

Table III summarizes the results of oxidizing the various phosphines with 96% nitric acid. In all cases but one, crystalline derivatives were prepared. It was found that nitric acid oxidized the carbon atom in the 3 position in 3-hydroxypropylphosphine to a carboxy group as well as oxidizing the phosphorus to a phosphonic acid group. However when this phosphine was treated with 30%w. hydrogen peroxide at 100° only the phosphorus atom was oxidized and 3-hydroxypropanephosphonic acid was obtained. The titration curves obtained during the course of the equivalent weight determinations gave further proof of the structures of the acids as all phosphonic acids gave two end-points, except 2-carboxyethanephosphonic acid which gave three, and all phosphinic acids gave one end-point.

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# Thermal Decomposition of Sulfur Compounds. I. 2-Methyl-2-propanethiol

BY C. J. THOMPSON, R. A. MEYER AND J. S. BALL[1]

2-Methyl-2-propanethiol was thermally decomposed in a quartz tube utilizing a flow method. The conditions (300–500° with exposure times of 10–120 seconds) employed in this study resulted in decompositions ranging from 0 to 97%. The predominant sulfur-containing decomposition product was hydrogen sulfide. In addition small amounts of elemental sulfur and residual sulfur were found. Isobutylene and isobutane were the major gaseous hydrocarbons produced. A free radical chain type decomposition mechanism is proposed.

2-Methyl-2-propanethiol was decomposed in a quartz tube under various conditions of time and temperature. The temperatures employed were 300, 350, 400, 450 and 500°, with residence times of 10 to 120 seconds. These conditions resulted in decompositions ranging from 0 to 97%. The decomposition at temperatures above 500°, where secondary reactions become preponderant, was not studied. Satisfactory sulfur balances were obtained, and results were found to be reproducible. Hydrogen sulfide, elemental sulfur, and residual sulfur (compounds unreactive to ordinary reagents) were found as decomposition products in addition to the gaseous hydrocarbons, isobutylene and isobutane. The amount of decomposition increased with each rise in temperature and/or time of exposure. Based on experimental evidence and supported by similar known reactions, a free radical decomposition mechanism is proposed.

## Apparatus and Procedure

**Materials.**—The 2-methyl-2-propanethiol was 99.92 mole % pure, as determined by the freezing point method of Rossini.[2] All other reagents were C.P. grade or better.

**Apparatus.**—The decompositions were made in a 25-mm. o.d. quartz tube heated by a 3-unit Hevi Duty organic combustion furnace. The heated section of the furnace was 560 mm. in length and contained a 27-mm. i.d. copper tube which acted as a heat distribution jacket and also as a support for the reaction tube. The entire furnace was covered

with an asbestos blanket 3 mm. in thickness. Individual temperature control on each of the 3 furnace units was achieved by the use of a 3-point Celectray controller employing chromel–alumel thermocouples located in recesses in the copper tube. The thermocouples were protected from the direct heat of the furnace elements by thin pads of asbestos. The entire furnace and reaction tube were inclined at an angle of 7.5° from the horizontal. The sample was fed into the upper end of the decomposition tube by a positive feed mechanism. This feed device consisted of a hypodermic syringe and an eccentric and rachet drive, the shaft of which pushed on the plunger of the syringe. The hypodermic needle attached to the syringe was inserted into the reaction tube through a neoprene stopper. The speed of the motor, the number of teeth engaged per revolution, and the size of the syringe were all variable. Feed rate was, therefore, variable from 0.04 to 1.75 g./min. A 125-mm. section of the reaction tube extending from the lower end of the furnace was packed with glass wool. Two slant-tube gas scrubbers (Fig. 1) were used in series at the exit end of the decomposition tube. These scrubbers each contained 100 ml. of 33% sodium hydroxide, which removed any hydrogen sulfide or thiol. This apparatus was designed to give complete gas scrubbing with very little back pressure. Test runs proved its ability to quantitatively remove hydrogen sulfide and thiol from the exit gases. Low-boiling hydrocarbons in the exit gases from the scrubbers were condensed in a trap cooled with a mixture of Dry Ice, carbon tetrachloride and chloroform. An A.S.T.M. Lamp Sulfur Apparatus, a Beckman Laboratory Model pH Meter, and a Consolidated Model 21-102 Mass Spectrometer were also used.

**Procedure. (a) Temperature Calibration.**—The temperature of the reaction tube was determined by a thermocouple placed equidistant from the walls of the tube. Readings were taken at 1-inch intervals and averaged to find the reported decomposition temperature. Temperature surge at any one point within the reaction tube was not greater than ±1.5°. All calibrations were made in an empty tube,

(1) To whom inquiries regarding this article should be sent.
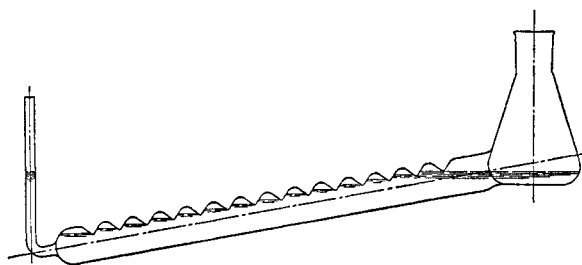(2) F. D. Rossini, Anal. Chem., 20, 110 (1948).

Fig. 1.—Slant tube gas scrubber.

but little temperature change was noted upon feeding the sample in at the most rapid rate used.

(b) **Residence-Time Calibration.**—This calibration was made with a special tube designed to have the same heated volume as the reaction tube, but with a minimum volume between the end of the furnace and a trap filled with aqueous silver nitrate solution. Residence time was defined as the interval between the start of the feed and the discoloration of the silver nitrate due to reaction with the hydrogen sulfide and/or thiol as they reached the end of the furnace. Check runs were, in all cases, reproducible within 1%.

(c) **Decomposition Procedure.**—After proper calibrations were made, the reaction tube, scrubbers, and cold trap were cleaned, reassembled, and swept with nitrogen for 5 minutes. A hypodermic syringe containing 10 to 15 ml. of 2-methyl-2-propanethiol was carefully weighed on an analytical balance and placed in the feed mechanism previously described. Eight to 10 ml. of the sample was then fed into the reaction tube at the predetermined rate, and the hypodermic syringe was reweighed to determine the exact quantity of sample added. The reaction tube, scrubbers and cold trap were then swept with nitrogen for 10 minutes.

**Analysis of Products.**—(a) Products remaining in the reaction tube or caught by the glass wool plug were diluted with methyl ethyl ketone and benzene to an accurate volume. 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.[3]

(b) The liquid in the two slant-tube gas scrubbers was diluted to 1000 ml. and a suitable aliquot taken for potentiometric determination of hydrogen sulfide and thiol. The method used was that of Tamele, Ryland and Irvine[4] modified to include hydrogen sulfide determination. Hydrogen sulfide was precipitated at a considerably more negative potential, and there was a sharp break in cell e.m.f. between its precipitation and the precipitation of the thiols. Exhaustive testing proved this method to be both precise and accurate. Potentials were measured with 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 2-methyl-2-propanethiol. These data were obtained by the decomposition of the pure sulfur compound in a quartz tube. Studies on the pure material appear desirable, as dilution with hydrocarbons would complicate the analysis and influence the mode and extent of the decomposition. The quartz tube was used to minimize catalytic effects.

The material reported as residual sulfur was a red to black viscous liquid with a sulfur content of approximately 67%. This material was found in increasing amounts as the severity of the cracking conditions was increased.

From Table I curves were derived, Figs. 2 through 4, which show sulfur distribution as a func-

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

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

TABLE I

SUMMARY OF DECOMPOSITION EXPERIMENTS ON 2-METHYL-2-PROPANETHIOL

| Temp., °C. | Feed rate, g./min. | Residence time, seconds | Per cent sulfur as RSH | H₂S | Free S | Resid-ual S | Sulfur recovery, % |
|---|---|---|---|---|---|---|---|
| 300 | 0.0674 | 120.00 | 93.1 | 0.0 | 0.0 | 0.0 | 93.1 |
| 350 | 1.6578 | 10.00 | 95.8 | 0.0 | .0 | .0 | 95.8 |
| 350 | 0.4102 | 30.00 | 95.0 | .6 | .0 | .0 | 95.6 |
| 350 | .4142 | 29.71 | 97.8 | .4 | .1 | .0 | 98.3 |
| 350 | .1724 | 60.00 | 86.7 | 9.7 | .5 | .0 | 96.9 |
| 350 | .0502 | 120.00 | 23.8 | 66.8 | 2.8 | 1.0 | 94.4 |
| 375 | .4259 | 25.00 | 62.7 | 27.7 | 2.2 | 0.0 | 92.6 |
| 375 | .2959 | 30.00 | 43.6 | 46.5 | 2.5 | 0.4 | 93.0 |
| 375 | .1283 | 60.00 | 22.0 | 73.2 | 3.3 | 1.5 | 91.7 |
| 400 | 1.4885 | 10.00 | 92.6 | 3.4 | 0.2 | 0.0 | 96.2 |
| 400 | 1.5112 | 9.85 | 89.4 | 4.2 | 0.3 | 0.2 | 94.1 |
| 400 | 0.6757 | 20.00 | 63.7 | 26.4 | 1.7 | 1.2 | 93.0 |
| 400 | .4806 | 20.00 | 57.5 | 29.9 | 2.3 | 0.2 | 89.9 |
| 400 | .4859 | 25.00 | 54.0 | 34.3 | 2.8 | 1.9 | 93.0 |
| 400 | .4295 | 25.00 | 44.1 | 41.9 | 3.2 | 0.9 | 90.1 |
| 400 | .3568 | 30.00 | 24.8 | 67.5 | 1.9 | 1.8 | 96.0 |
| 400 | .3589 | 29.83 | 24.6 | 67.1 | 2.1 | 2.0 | 95.8 |
| 400 | .2858 | 30.00 | 24.8 | 64.6 | 3.1 | 1.0 | 93.5 |
| 400 | .1445 | 60.00 | 12.4 | 79.5 | 1.6 | 3.0 | 96.5 |
| 400 | .1457 | 59.50 | 12.4 | 77.6 | 1.8 | 3.1 | 94.9 |
| 425 | 1.0946 | 10.00 | 60.6 | 29.8 | 2.1 | 0.2 | 92.7 |
| 425 | 0.8341 | 15.00 | 38.3 | 52.7 | 3.4 | .6 | 95.0 |
| 425 | .5232 | 20.00 | 17.8 | 72.3 | 4.0 | .8 | 94.9 |
| 450 | 1.2286 | 10.00 | 30.7 | 59.7 | 1.6 | 2.3 | 94.3 |
| 450 | 0.2846 | 30.00 | 8.1 | 79.9 | 2.2 | 3.8 | 94.0 |
| 450 | .2849 | 29.97 | 8.0 | 79.9 | 1.8 | 4.5 | 94.2 |
| 450 | .0848 | 60.00 | 2.8 | 84.4 | 2.3 | 5.4 | 94.9 |
| 450 | .0861 | 59.13 | 2.1 | 83.1 | 3.7 | 5.0 | 93.9 |
| 500 | 1.1703 | 10.00 | 7.7 | 81.2 | 1.2 | 3.7 | 93.8 |
| 500 | 1.1761 | 9.95 | 10.2 | 79.5 | 0.6 | 4.1 | 94.4 |
| 500 | 0.2242 | 30.00 | 2.9 | 86.0 | 1.1 | 4.3 | 94.3 |

tion of residence time for the three temperatures. The values recorded on the graphs were obtained from the table after prorating the loss. Justification for this proration is readily evident in the two runs where no decomposition occurred.
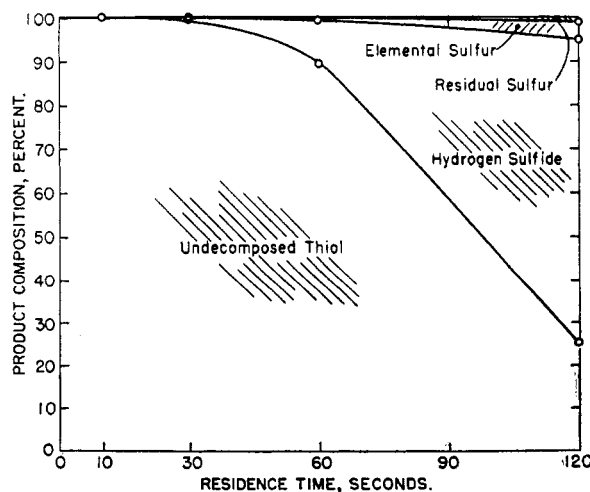
The reproducibility of the work can be observed



Fig. 2.—Effect of residence time on sulfur distribution at 350°.
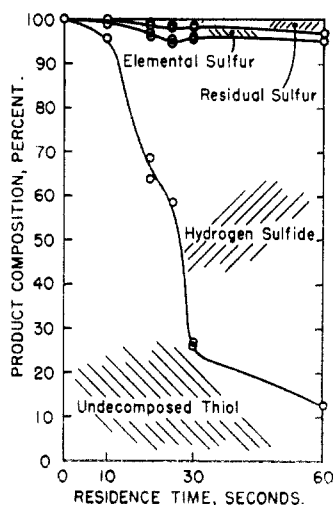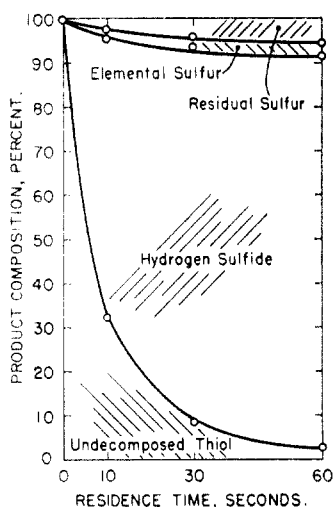
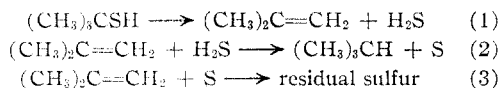Fig. 3.—Effect of residence time on sulfur distribution at 400°.



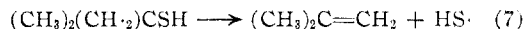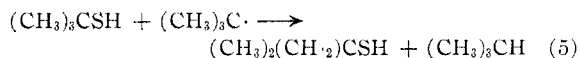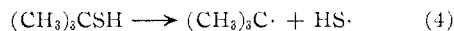Fig. 4.—Effect of residence time on sulfur distribution at 450°.

by comparing, in Table I, runs obtained at the same temperature and residence time. The data are in good agreement when proper allowance is made for the slight fluctuations in feed rate.

Some of the runs were made after extensive furnace modifications. This work included rearrangement of the units and removal of four spacer plates, thus shortening the length of the heated section by 2 inches. Some variation in feed rate and decomposition is reflected by these modifications.

The products formed indicate that the over-all reactions are

$$(CH_3)_3CSH \longrightarrow (CH_3)_2C=CH_2 + H_2S \quad (1)$$
$$(CH_3)_2C=CH_2 + H_2S \longrightarrow (CH_3)_3CH + S \quad (2)$$
$$(CH_3)_2C=CH_2 + S \longrightarrow residual\ sulfur \quad (3)$$

The rapid increase in rate of the reaction (Fig. 4) and the formation of complex tarry products suggests the presence of a free radical mechanism such as that proposed by Malisoff and Marks.[5] This mechanism for the reaction shown as (1) may be formulated

(5) W. M. Malisoff and E. M. Marks, Ind. Eng. Chem., 23, 1114 (1931).

$$(CH_3)_3CSH \longrightarrow (CH_3)_3C\cdot + HS\cdot \quad (4)$$
$$(CH_3)_3CSH + (CH_3)_3C\cdot \longrightarrow$$
$$(CH_3)_2(CH\cdot_2)CSH + (CH_3)_3CH \quad (5)$$
$$(CH_3)_3CSH + HS\cdot \longrightarrow (CH_3)_2(CH\cdot_2)CSH + H_2S \quad (6)$$
$$(CH_3)_2(CH\cdot_2)CSH \longrightarrow (CH_3)_2C=CH_2 + HS\cdot \quad (7)$$

Reactions (5) and (6) produce the same free radical. As shown in reaction (7) it breaks down to give an HS· radical which may re-enter reaction (6) thus giving the chain-forming step.

Analysis of the hydrocarbon gases shows a decrease in the butane/butene ratio as the reaction proceeds. This is in conformity with the proposed mechanism as reaction (5) producing isobutane is not a chain reaction while reactions (6) and (7) producing isobutylene are. The rapid increase in hydrogen sulfide formation is also predicted by reactions (6) and (7).

The mass spectrometer pattern for 2-methyl-2-propanethiol (see Fig. 5) indicates that the carbon–sulfur bond is susceptible to cleavage. The high 57 peak observed is the parent peak less 33 and is indicative of the split into the two fragments $(CH_3)_3C$ and $SH$.
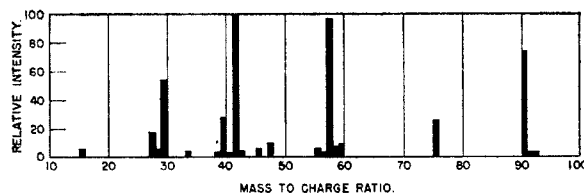


Fig. 5.—Mass spectra of 2-methyl-2-propanethiol.

The "toluene carrier gas" technique[6] for the detection of free radicals was employed in an attempt to prove the mechanism of decomposition. The conditions of temperature, pressure and flow rate were similar to those used in a normal decomposition run. Under these conditions secondary reactions became so troublesome that this technique proved to be unsatisfactory for establishing the reaction mechanism. If the pressure were decreased and the flow rate and dilution increased as suggested by the method, the initial decomposition temperature would be raised more than 100°. Possibly the presence of free radicals could be detected at the higher temperatures, but this would not prove the presence of free radicals during ordinary thermal decomposition at the lower temperatures.

The decomposition curve as shown in Fig. 2 suggests an induction period of some 60 seconds before the chain mechanism is contributing to an appreciable extent. At 400° the induction period is much shorter and the decomposition is proceeding primarily by the chain reaction. At 450°, Fig. 4, there is no measurable induction period with the decomposition being controlled almost entirely by the chain reaction. The low concentration of undecomposed thiol explains the leveling off of the curves in Figs. 3 and 4 at residence times of 30 to 60 seconds.

Reaction (2) can be written as a free radical mechanism, but this adds little to its understanding. It appears also to be reversed in some instances.

(6) M. Szwarc, Chem. Revs., 47, 75 (1950).

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.

**Acknowledgments.**—This work was done under a coöperative agreement between the Bureau of Mines, United States Department of Interior, and
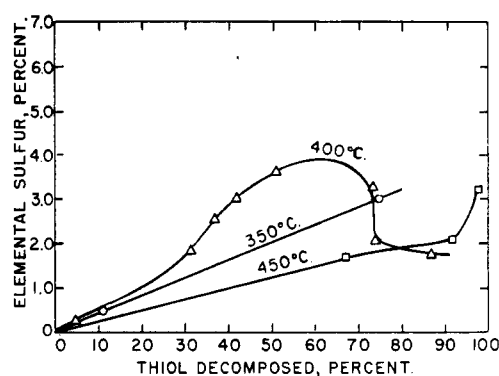


Fig. 6.—Elemental sulfur resulting from thiol decomposition at temperatures of 350, 400 and 450°.

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

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# Thermal Decomposition of Sulfur Compounds. II. 1-Pentanethiol

BY C. J. THOMPSON, R. A. MEYER AND J. S. BALL[1]

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 authors[2] 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 as 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 resistance 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

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(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).