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H. Austin Taylor and Edwin T. Layng

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The Thermal Decomposition of Propyl Mercaptan

H. AUSTIN TAYLOR AND EDWIN T. LAYNG,[1] *New York University*

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The thermal decomposition of normal propyl mercaptan over a temperature range from 405 to 435°C and pressures from 100 to 300 mm is homogeneous on a poisoned glass surface. The reaction is complex showing an induction period with auto-accelerating rate, ending finally in a pseudo-equilibrium involving propylene, hydrogen sulphide and isopropyl mercaptan. The energy of activation of the induction period is about 40,000 calories and that of the later reaction 39,000 calories. A mechanism, has been proposed which involves primarily the formation of propyl sulphide reacting further to form a sulphonium hydrosulphide as an unstable intermediate.

FROM a recent study of the decomposition of ethyl mercaptan Trenner and Taylor[2] concluded that the mechanism involved a series of consecutive reactions leading to an equilibrium in which ethylene and hydrogen sulphide preponderate. The marked similarity in the decomposition of ethyl sulphide suggested a parallel mechanism and the same intermediate was tentatively assigned to both reaction schemes. The isolation of this intermediate could not be accomplished as definite proof of the conclusions drawn. Propyl mercaptan being homologous with the ethyl derivative a similarity in their decompositions might logically be expected whilst the individual rates of the consecutive reactions might be such as to allow the isolation of the intermediate compound for further study. Although this has not been achieved the work has served to verify, amplify or in some ways modify the conclusions previously drawn.

EXPERIMENTAL

The sample of normal propyl mercaptan used was from the Eastman Kodak Company and was carefully dried and fractionated to give a product boiling in agreement with the findings of Ellis and Reid[3] from 67.4 to 67.6°C at 763 mm.

A. Static method

The apparatus used in the work was practically identical with that used by Trenner and Taylor. The reaction vessel of Pyrex glass had a capacity of 279 cc. The total free volume outside the furnace was less than two percent of this value and was maintained by auxiliary heaters at 65°C to prevent condensation of mercaptan. As was found with ethyl mercaptan the induction periods in the decomposition of the propyl mercaptan were somewhat erratic in duration on a clean surface but after three or four samples were successively decomposed, the products of each being removed by five minutes pumping with a "hyvac" oil pump, the induction periods as well as the entire decomposition rates could be reproduced at will. The results for various pressures and temperatures will be presented later.

B. Dynamic method

To obtain a qualitative knowledge of the products of reaction particularly during the early stages, as substantiation of the proposed mechanism, several dynamic experiments were made. The propyl mercaptan was maintained at a temperature of 78°C with ethyl alcohol constantly refluxing, to exert a constant vapor pressure on a calibrated capillary connected with the reaction tube in the furnace. The temperature was measured by a platinum resistance thermometer located in the center of the reaction tube. Passing out of the reaction tube the gases were carried through three traps. The first trap was immersed

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1933.

[2] Trenner and Taylor, J. Chem. Phys. 1, 77 (1933).

[3] Ellis and Reid, J. Am. Chem. Soc. 54, 1674 (1932).

in a Dewar flask containing ice and salt at −19°C; the second was immersed in solid carbon dioxide and toluene and the third in liquid air. This latter trap was connected to a mercury manometer and gas burette. The pressure on the reservoir side of the calibrated capillary was thus constant at 1066 mm, the rest of the system being maintained at atmospheric pressure. That the system should be entirely free from oxygen, it was first swept out with helium. During a run as the helium was displaced it was allowed to blow off at atmospheric pressure, whilst any small quantities remaining would not interfere with a qualitative analysis of other gases produced by reaction.

RESULTS

Since there are no data available on the vapor pressure of propyl mercaptan and since the apparatus for the static experiments lent itself admirably to this determination the values given in Table I were obtained.

TABLE I.

Temperature		Vapor pressure	
284.6°K	318.1°K	84.0 mm	351.0 mm
289.9	323.3	97.5	425.0
295.8	328.2	141.0	509.5
301.7	333.3	182.4	600.0
307.5	340.57 (calc'd)	233.0	760
313.0		284.2	

Fig. 1 shows these results graphically where the logarithm of the pressure is plotted against the reciprocal of the absolute temperature. The

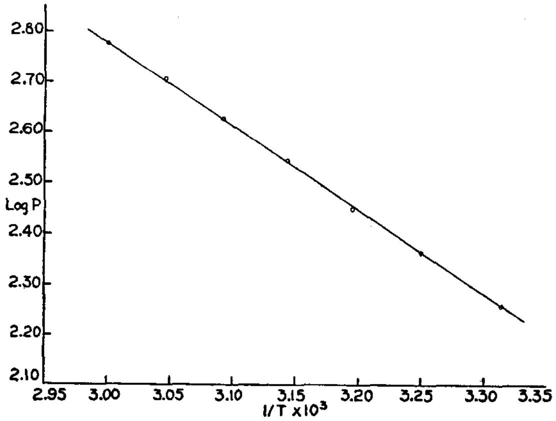


FIG. 1. Vapor pressure curve of propyl mercaptan.

straight line may be represented by the following equation:

$$\log p = -1647/T + 7.7190.$$

A. Static method

By this method data on the rate of decomposition were obtained at varying pressures from 100 to 350 mm and at temperatures from 405 to 435°C. Fig. 2 illustrates graphically the rates obtained at initial pressures of 101, 152, 199, 300 and 351 mm at 405°C. It will be observed that the curves are identical in form to those obtained by Trenner and Taylor for ethyl mercaptan. Since it was there shown that the point of inflection was of considerable importance, its exact location was made experimentally by taking pressure readings every fifteen seconds in the neighborhood of the approximate position of maximum rate previously determined. Table II gives the location of the points of inflection at the various pressures and temperatures studied. The last two columns will be referred to later in the discussion.

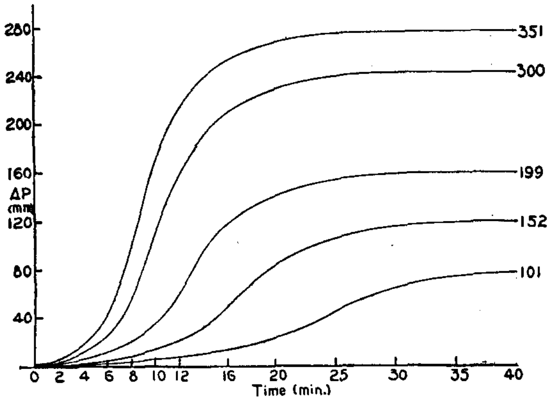


FIG. 2. Decomposition rate curves of propyl mercaptan at pressures of 101, 152, 199, 300 and 351 mm at 405°C.

The peculiar behavior of the induction period previously mentioned, suggesting heterogeneity, the effect of an increased surface was tested. Results again identical with those for ethyl mercaptan were found. The first reaction after the chamber had been filled with short lengths of Pyrex tubing and very thoroughly evacuated showed practically no induction period. In subsequent reactions this became progressively

TABLE II.

Init. press. P (mm)	Time to inflection (min.)	Press. increase	Press. unreacted P_I	P_I/P
Temperature 405°C				
351	8.75	132	219	0.624
300	10.00	107.6	192.4	0.641
199	12.75	71.8	127.2	0.638
152	17.50	60.7	91.3	0.601
101	25.00	41.5	59.5	0.589
Temperature 415°C				
351	5.50	134	217	0.618
304	6.12	107.5	196.5	0.646
202	9.00	85	117	0.585
149	13.00	63.5	85.5	0.574
99	19.00	44.7	54.3	0.554
Temperature 425°C				
351	3.75	132	219	0.624
297	4.00	111.9	185.1	0.624
200	5.75	88	112	0.560
147	9.00	63.6	83.4	0.569
101	12.00	45.5	55.5	0.550
Temperature 435°C				
347	2.50	133	214	0.617
298	2.75	109	189	0.634
202	3.75	85.9	116.1	0.581
150	6.00	67.2	82.8	0.552
100	8.00	43.8	56.2	0.562

TABLE III.

Init. press. (mm)	Press. increase	Percent decomp.	t_{25}	t_{50} (min.)
Temperature 405°C				
351	276	78.6	1.13	2.55
300	243	81.0	1.26	2.91
199	164	82.0	1.42	3.30
152	126	82.8	1.72	4.27
101	86	85.3	1.85	4.35
Temperature 415°C				
351	279	79.5	0.76	1.75
304	247	81.3	0.80	1.84
202	166	82.3	0.97	2.32
149	125	83.9	1.30	2.75
99	86	86.0	1.56	3.42
Temperature 425°C				
351	283	80.7	0.50	1.15
297	242	81.5	0.55	1.29
200	165	82.5	0.62	1.62
147	125	85.0	0.92	2.47
101	87	87.0	1.12	2.78
Temperature 435°C				
347	281	81.2	0.36	0.85
298	244	81.7	0.37	0.85
202	168	83.2	0.42	1.02
150	130	87.0	0.60	1.77
100	89	89.0	0.91	2.10

longer eventually reaching a constancy to duplicate that found for the empty vessel. This same "aging" effect was shown also when finely powdered glass was used to increase the surface. It is apparent therefore that the reaction is one which may be catalyzed under suitable conditions but that under the conditions prevalent in this work is strictly homogeneous. The slope of the rate curves subsequent to the inflection was always constant even for reactions in a new vessel before aging. This fact would suggest that the secondary reactions are always homogeneous. That the primary reaction becomes homogeneous may be connected with the observed darkening of the reaction bulb by a dark brown deposit which could be distilled slowly under vacuum and which therefore could not be carbon but in all probability was a complex polysulphide.

An examination of the end-points of the reaction shows a variation with temperature and pressure. The greatest percentage decomposition occurred at the highest temperature and lowest initial pressure; the least percentage decomposition at the lowest temperature and highest pressure. This variation is apparent from the data in Table III and would suggest the existence of an equilibrium similar to that established by Trenner and Taylor for ethyl mercaptan, ethylene and hydrogen sulphide. In an attempt to verify the existence of this equilibrium for propylene and hydrogen sulphide a mixture of 350 mm of the latter and 355 mm of the former were allowed to react at 435°C. Such a mixture should be equivalent to 350 mm propyl mercaptan which decomposed under these conditions with a pressure increase of 81.2 percent. If the suggested equilibrium existed, the mixture should react with a pressure decrease of 18.2 percent. Actually a maximum decrease of only 10 percent was obtained after twelve hours, after which time the pressure began to increase again very slowly. Duplicate runs always showed the same tendency though quantitative reproducibility was small suggestive of some heterogeneity in the complicating reactions.

The effects of foreign gases were determined in eleven cases with oxygen, ethylene, propylene, sulphur dioxide, carbon dioxide, nitrogen, helium,

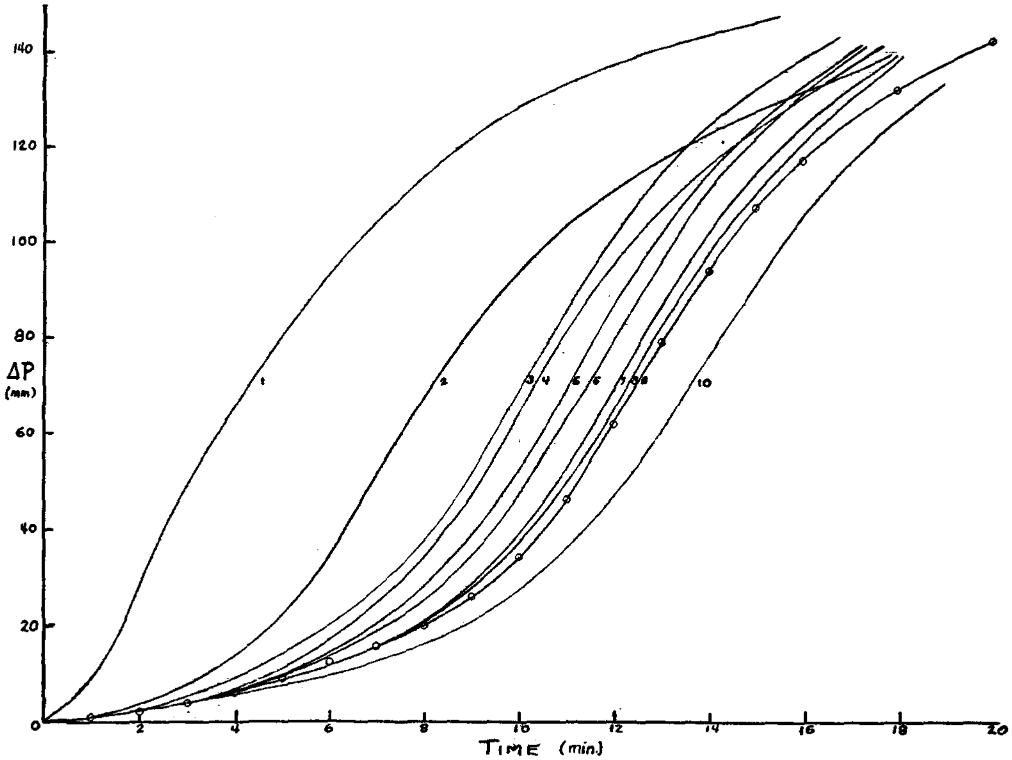


FIG. 3. Foreign gas effect. Initial pressure of PrSH = 200 mm. Temp. = 405°C

1. 5 mm O_2
2. 102 mm C_2H_4
3. 102 mm CO_2
4. 100 mm C_3H_6
5. 100 mm N_2
6. 100 mm H_2S
7. 100 mm C_2H_6
8. 100 mm H_2
9. Normal
10. 101 mm NH_3

hydrogen sulphide, ethane, hydrogen and ammonia. In each instance, oxygen excepted, 100 mm of gas were added to 200 mm of mercaptan vapor. With oxygen only 5 mm were used because of the pronounced effect it had on the length of the induction period. Fig. 3 shows eight of the eleven cases studied, the normal rate curve being included for comparison. The curve for sulphur dioxide is practically coincident with that for carbon dioxide, whilst helium was apparently without effect. The striking feature of Fig. 3 is the parallelism of the curves beyond the inflection in each case, ethylene and propylene excepted, the sole differences lying in the lengths of the induction periods. The more specific effects of the products of decomposition were determined by allowing a sample of mercaptan partially to decompose and then adding a fresh sample and following the reaction to the end. By knowing from previous experiment the shape of the reaction rate curve for the initial sample, the rate curve for the injected sample may be synthesized by subtracting the ordinates of the curve for the initial sample alone from those of the actual observed curve. Three such tests were made and checked: first, the fresh reactant was added before the original sample had reached the maximum reaction rate, that is, early in the induction period; second, the addition made at the point of inflection; and third, injecting the second sample when the first had practically completely decomposed. The results of these three tests are condensed on one diagram in Fig. 4 for the sake of simplifying comparison. The points where the injections were made have been taken as origins for axes for the injected sample. The continuous curve marked "normal" represents the course of decomposition of 181 mm of mercaptan at 405°C. The first injection of 172 mm was made when the original 181 mm had

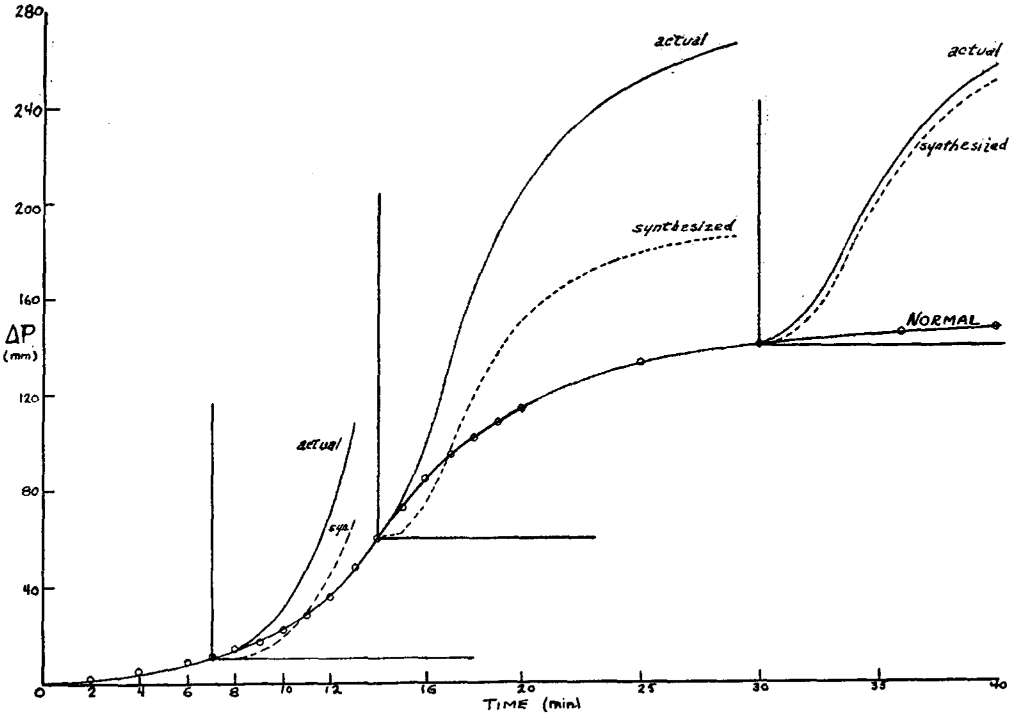


FIG. 4. Composite diagram of the effects of three separate additions of propyl mercaptan to 181 mm already partially decomposed at 405°C. Sample 1 of 172 mm injected after 7 min. Sample 2 of 177 mm injected after 14 min. and sample 3 of 181 mm, after 30 min.

reacted for seven minutes. The curve labelled "actual" represents the course of decomposition of the combined samples. By subtracting the ordinates of the normal curve from those of the actual curve the synthesized curve for the injected sample is found and is shown dotted in the diagram. In the second case 177 mm were injected after 181 mm had decomposed 14 minutes and in the third case 181 mm were injected at the thirtieth minute of decomposition of the original 181 mm. It should be noted that the induction period of the injected sample is in each instance shorter than that of the original sample. The most marked shortening occurs however in the sample injected at the point of inflection of the original sample.

It was shown by Trenner and Taylor that the decompositions of ethyl mercaptan and ethyl sulphide proceeded analogously and were in all probability intimately connected. Since propyl sulphide boils at 142°C it was impossible with the present apparatus to make any extended study of its decomposition due to the inability of keeping the stopcocks and capillaries at this elevated temperature. Nevertheless by maintaining the capillaries at 75°C a few observations at initial pressures between 30 and 60 mm and at temperatures between 435 and 455°C were made. Examples of the curves obtained are shown in Figs. 5 and 6. The lower curve in Fig. 5 is for the decomposition of 31 mm of propyl sulphide at 435°C. The shape is essentially the same as that found for low pressures of mercaptan. Although the marked flattening at these pressures appears to mask the presence of the induction period the fact is that the curve is practically all induction period, the rate of reaction never becoming sufficiently great to produce a noticeable point of inflection. There is no doubt that at higher pressures the curves would show the same hysteresis shape that mercaptan shows. This can be seen from Fig. 6 where curve 1 is for 30 mm of mercaptan and curve 2 for 31 mm of sulphide both at 435°C where the mercaptan curve is so flattened as to indicate an apparently smooth decomposition free from induction.

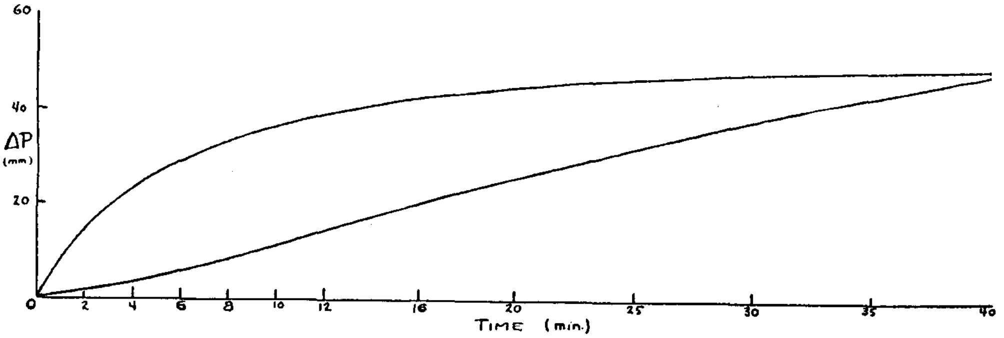


FIG. 5. Decomposition rate curves of propyl sulphide (lower) and propyl sulphide and hydrogen sulphide (upper).

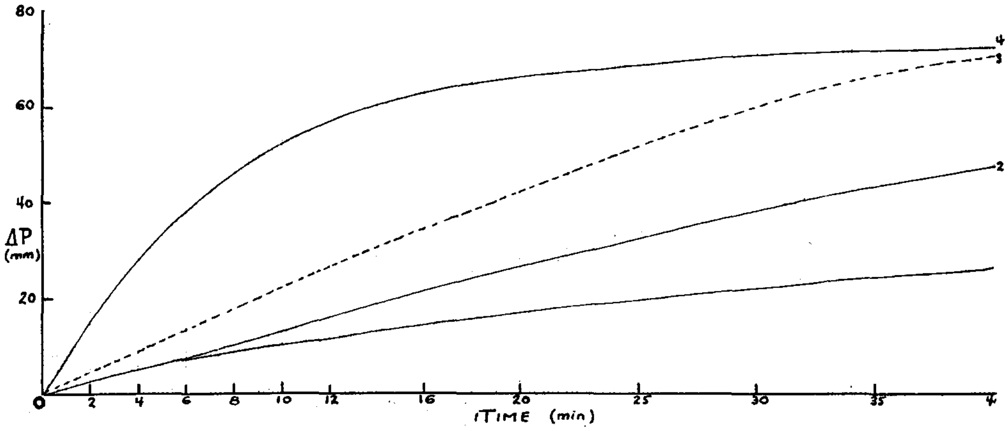


FIG. 6. Rate curves for the decomposition of (1) propyl mercaptan, (2) propyl sulphide, (4) a mixture of both. Curve (3) for comparison is the result of adding the ordinates of (1) and (2).

Since with ethyl sulphide it was shown that the presence of hydrogen sulphide completely removed the induction period a comparison was made in this case with propyl sulphide. Fig. 5 shows the result at 435°C, the upper curve representing the pressure change with time of 30 mm each of propyl sulphide and hydrogen sulphide. The lower curve for comparison is that of 31 mm propyl sulphide alone. The shape of the former curve is entirely different from that of the latter; there is no induction period, the reaction beginning at maximum rate. It should be noted in passing that hydrogen sulphide alone is stable at 435°C.

Since mercaptans are in reality substituted hydrogen sulphides it might be expected that mixtures of sulphides with mercaptan would behave as did mixtures with hydrogen sulphide. In Fig. 6 are given the results observed at 435°C for a mixture of 32 mm propyl sulphide and 31 mm propyl mercaptan indicated by curve 4. Curves 1 and 2 as already stated are for 30 mm mercaptan and 31 mm sulphide alone, respectively. The dotted line, curve 3, is simply the sum of the ordinates of curves 1 and 2 and is thus the pressure change which would be expected for the mixture if each constituent reacted individually. The marked difference between the observed curve 4 and the "theoretical" curve 3 must surely indicate an interaction in some way between the sulphide and mercaptan as between the sulphide and hydrogen sulphide. Similar results were found also at 445° and 455°C.

B. Dynamic method

Experiments were made at temperatures of 405°, 435° and 440°C. The contact times under the conditions previously given were calculated to be 0.97, 0.93 and 0.92 minute, respectively, at these temperatures, all estimated to be well within the induction period of a reaction with an initial pressure of 760 mm.

In the first run at 405°C all of the reaction products condensed in the first trap at −19°C as a colorless liquid which distillation proved to be unchanged mercaptan. There had been therefore practically no reaction. At 435°C the majority of the products condensed again in the first trap, there being, however, a small amount of liquid in the carbon dioxide trap. This latter proved to be only liquid hydrogen sulphide by the usual tests. The liquid in the first trap was washed with sodium hydroxide, most of it dissolving. The alkali-insoluble, oily residue was separated by extraction with ether and the ether removed by distillation. An amount of a brownish liquid remained, too small to be tested but having the disagreeable odor of propyl sulphide. The alkali-soluble portion was acidified with dilute hydrochloric acid liberating a lemon colored liquid which practically all distilled in the range for propyl mercaptan leaving a small amount of a tarry residue which showed no boiling point but seemed to decompose at about 200°C.

At 440°C the first trap at −19°C contained a large amount of a brown liquid, the second at −78°C, a considerable quantity of a colorless liquid, the liquid air trap was empty and no uncondensed gases were collected in the gas burette. The contents of the first trap were treated as before. The alkali-insoluble portion, again a brownish oily liquid with an odor of propyl sulphide, was treated with mercuric chloride solution to yield a finely divided crystalline precipitate of buff color, which was taken to be the white addition compound of propyl sulphide and mercuric chloride colored with traces of polysulphides, the presence of which was indicated by a distillation with decomposition above 200°C. The alkali-soluble portion proved again to be unchanged mercaptan contaminated also with polysulphides which decomposed about 200°C. The colorless liquid in the carbon dioxide trap proved to be hydrogen sulphide and hydrocarbons. The hydrogen sulphide was allowed partially to distill off and the trap then connected to an Orsat gas analyzer. A large fraction of the gas was absorbed by sodium hydroxide, another large fraction by bromine water and the small remainder by absolute alcohol. The gas removed by sodium hydroxide was undoubtedly hydrogen sulphide. The bromine water would remove propylene whilst absolute alcohol would take up propane. Boiling points will substantiate these conclusions since that of hydrogen sulphide is −59°C, that of propylene −47°C and of propane −44.5°C. Lower paraffins and olefines are excluded since they would not condense at −78°C. It must be admitted that higher hydrocarbons would be retained but their probability of formation seems remote.

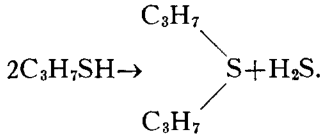
Discussion of Mechanism

The marked analogy between the foregoing data and those found by Trenner and Taylor for ethyl mercaptan would suggest a similar mechanism of decomposition for propyl mercaptan. The presence of the induction period is indicative of at least two reactions occurring during the decomposition and most obviously a distinction can be made between the two portions of the reaction up to and succeeding the point of inflection. That this latter is a comparable point for all the cases studied can be seen from a perusal of the last column of Table II in which the ratio of the pressure of mercaptan undecomposed to the initial pressure is constant and independent of the temperature. This fact makes it possible to study separately the course of the reaction in its later stages with the point of inflection as origin for this portion. It was on this basis that the fractional lives given in Table III were calculated. Because of the variable end-point of the reaction at different pressures and temperatures, an approximate correction has been applied to make the times more comparable from case to case. To do this the end-point of the reaction at the highest pressure for each temperature was chosen as standard and all the other end-points at this temperature corrected to this value by multiplying each by the ratio of the percentage increase of this standard reaction to that of the particular reaction to be corrected. The quarter and half lives so found will be seen to show approximate constancy with, however, a definitely rising trend with decrease in initial pressure at each temperature. This would lead one to suspect that this secondary portion of the reaction constituted a pure unimolecular reaction which deviated from unimolecularity around 300 mm. It is probable however as will be shown that even this portion of the overall rate curve is not typical of a simple reaction and that therefore these fractional lives are themselves complex.

The energy of activation of this secondary part of the reaction calculated from the above fractional lives by means of the Arrhenius equation is found to have an average value of 39,000 calories. In a similar manner using the times taken to reach the points of inflection the energy of activation of the induction period may be calculated to be on the average 40,000 calories. The agreement between these two values is striking when it is considered that an error of one-hundredth of a minute in the fractional life will change the value of the energy of activation by almost 1000 calories. The agreement also has as a consequence the impossibility of separating the primary and secondary reactions by a temperature variation. The energy of activation of the reaction of mixtures of propyl mercaptan and propyl sulphide was calculated, using the quarter life, to be 39,500 calories, also in striking agreement with the previous values.

On the basis of these facts it is possible to postulate a probable mechanism for the reaction which will account for all the observations and at the same time suggest where complicating side reactions might mask a complete understanding of the reaction. It will be convenient to consider the reactions postulated individually, for since the mechanism formally resembles that of Trenner and Taylor for ethyl mercaptan some amplification is possible.

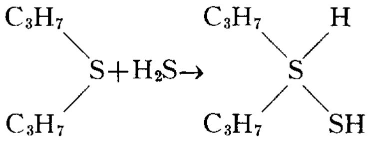
In the first place the induction period is viewed as being due to the bimolecular reaction of two propyl mercaptan molecules to give propyl sulphide and hydrogen sulphide without volume change:



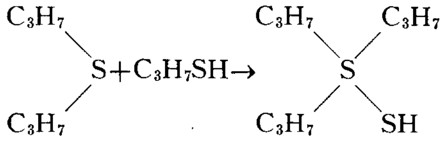
$$2C_3H_7SH \rightarrow (C_3H_7)_2S + H_2S.$$

Well known as a heterogeneous reaction on metallic sulphide surfaces it is probable that a clean glass surface would catalyze it and cause the observed erratic values in the length of the induction period. That hydrogen sulphide is formed early in the reaction has been shown by the results from the dynamic method at 435°C where it was further shown (the second case) to be present without any accompanying propylene or other hydrocarbon. Furthermore it may be recalled a small amount of an alkali-insoluble portion was also found. To split hydrogen sulphide from a mercaptan without forming any olefine would seem to require the above reaction which is in keeping with numerous previous findings.

For the next step, the observation that both hydrogen sulphide and propyl mercaptan were capable of removing completely the induction period of the decomposition of propyl sulphide, must mean that a definite chemical reaction occurs in which an addition compound is formed. Trenner and Taylor suggested such an intermediate formed from ethyl sulphide and hydrogen sulphide. Since propyl mercaptan has been shown to remove the induction period of the sulphide and since it must still be present in considerable quantities early in the reaction, there would appear to be two competitors for the propyl sulphide formed in the first step as shown by the following equations:



$$(C_3H_7)_2S + H_2S \rightarrow (C_3H_7)_2S(H)(SH) \qquad \text{(a)}$$



$$(C_3H_7)_2S + C_3H_7SH \rightarrow (C_3H_7)_2S(C_3H_7)(SH) \qquad \text{(b)}$$

The intermediate in Eq. (a), analogous to that which Trenner and Taylor postulated and attempted unsuccessfully to prepare in quantity, appears at first sight to be improbable. It is however, only by comparison with the compound in Eq. (b) that its possibility becomes apparent, for this latter compound would simply be tripropyl sulphonium mercaptan. Now although no such compounds are definitely reported in the literature there is every indication that they do exist. There has been reported[4] an analogous selenium compound $(C_2H_5)_2Se.SeH$. The sulphonium halides and hydroxides are well known, the latter being strong bases. Bernthsen and Sudborough[5] state specifically "trimethyl sulphonium hydroxide . . . gives salts with acids even with hydrogen sulphide, these latter closely resemble the alkali sulphides." Crum-Brown and Blaikie[6] succeeded in preparing trimethyl sulphonium sulphide $[(CH_3)_3S]_2S$ from equivalent amounts of trimethyl sulphonium hydroxide and hydrogen sulphide. Attempts to concentrate an aqueous solution by drying over phosphorus pentoxide were successful only to a certain point however, beyond which decomposition to dimethyl sulphide occurred.

In view of these facts a synthesis of triethyl sulphonium hydrosulphide was attempted.[7] Triethyl sulphonium bromide was treated with sodium hydrosulphide in absolute alcohol at 35°C. After some time the mixture assumed a yellow color and smelled strongly of mercaptan. A fractional distillation yielded ethyl mercaptan and diethyl sulphide. The presence of these compounds is in reality positive evidence that the desired sulphonium hydrosulphide had first been formed but decomposed rapidly. A second attempt using liquid hydrogen sulphide as solvent was unsuccessful because of the small solubility of sodium hydrosulphide. A substitution of ammonium hydrosulphide for the latter, however, despite its solubility in liquid hydrogen sulphide, showed no apparent reaction with the sulphonium bromide. Finally an attempt to prepare the analogous compound $(C_2H_5)_3S-SC_2H_5$ by treating sodium mercaptide with triethyl sulphonium bromide in absolute alcohol was without success. This inability to isolate the suggested compound indicates, in view of the existence of other parallel compounds, its marked instability, such that its immediate decomposition might be expected particularly under the experimental conditions used in the mercaptan decomposition studies.

The third step in the series would then involve the decomposition of the sulphonium hydrosulphide into propylene and hydrogen sulphide:

$$(C_3H_7)_3S-SH \rightarrow 3C_3H_6 + 2H_2S.$$

The rapidity of this reaction with its large pressure increase would most certainly counterbalance the pressure decrease in the second step of the scheme, namely, the formation of the intermediate. No pressure decrease was ever observed.

On the basis of this mechanism the production of polysulphides which are always found as a "tarry" residue receives a plausible explanation. The sulphonium hydrosulphide referred to above, being essentially a complex mercaptan can undergo the reaction in Step I to form complex sulphides by loss of hydrogen sulphide from two molecules. These complex sulphides in the presence of more mercaptan or of hydrogen sulphide would unite to form new mercaptans still more complex, a cyclic chain of reactions which could produce large molecules of high sulphur content. There is evidence from the dynamic runs that such tarry materials contain both mercaptan and sulphide linkages since part is soluble in alkali and part insoluble.

The absence of an induction period in the decompositions of propyl sulphide-hydrogen sulphide and propyl sulphide-propyl mercaptan mixtures as also its presence in propyl mercaptan alone is well accounted for. The initial step in the latter involves the formation of propyl sulphide and hydrogen sulphide; a reaction with no volume change giving therefore an induction in the rate of pressure increase. With the mixtures the formation of the intermediate and its subsequent rapid decomposition can immediately occur. In fact under the experimental conditions the rate of pressure increase must actually measure the rate of the bimolecular association with a pressure decrease in terms of the larger pressure increase of the much more rapid, probably unimolecular, decomposition of the intermediate. It is this counterbalancing of effects that probably gives to the fractional lives of the

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[4] Pieroni and Coli, Gazz. chim. ital. **44**, II, 353 (1914).

[5] Bernthsen and Sudborough, Organic Chemistry, pp. 93, 752. D. Van Nostrand Co. (1930).

[6] Crum-Brown and Blaikie, J. prakt. Chim. **23**, 400 (1881).

[7] The experimental work was kindly performed by Dr. Nelson R. Trenner to whom thanks are due.

later portions of the reaction the falling values with increasing pressure.

The decreased induction periods in the injection tests also receive explanation in this same way. Since propyl sulphide or some substances with similar thio-ether linkages, possibly of the polysulphide type, are produced in the decomposition of the initial mercaptan sample, the rate of the association reaction, Step II, would be increased by the addition of the injected mercaptan, and hence the overall rate of pressure increase, giving a decreased induction for the injected sample. The suggested mechanism would necessitate that the concentration of propyl sulphide formed from propyl mercaptan by Step I should be greatest at the point of inflection. This is in line with the observation that the decrease in the induction period is greatest for the sample injected at the point of inflection.

Finally, with regard to the equilibrium existing at the "end-point" of the decompositions, it has been pointed out that mixtures of propylene and hydrogen sulphide did not yield results in line with expectations from propyl mercaptan. This was shown to be due to the instability of propylene at these elevated temperatures. Duffey, Snow and Keyes have recently[8] studied the equilibrium between isopropyl mercaptan, propylene and hydrogen sulphide in presence of various catalysts at 275–300°C by a dynamic method. The rule of addition to unsaturated compounds would suggest that the $-SH$ group in hydrogen sulphide would add to the least hydrogenated carbon atom in propylene thus giving isopropyl mercaptan. It is this same equilibrium then, that should eventually be reached in normal propyl mercaptan decomposition. Keyes and coworkers experienced difficulty in overcoming propylene polymerization in presence of many of their catalysts, such that the same end-point was not reached from the two sides of the equilibrium. The amount of isopropyl mercaptan present at equilibrium from the decomposition reaction was always greater than that from the combination reaction.

To ascertain whether this propylene polymerization would account for the difficulties in the present work, a quantity of propylene was introduced into the reaction vessel at 435°C. A very slow reaction with a pressure decrease occurred. After twenty-four hours this decrease having reached a maximum, the pressure began to increase indicating depolymerization and decomposition. This is in keeping with the findings of Wheeler and Wood[9] who find similar polymerization followed by cracking. It would seem therefore, that a shift in the previously observed "end-point" of the propyl mercaptan decomposition should be noticeable after a long period of time due to the propylene reactions. To this end 300 mm of mercaptan were maintained at 435°C. After half an hour the pressure had increased 244 mm changing only one millimeter in the next half hour with no further change during the second hour. This is the value previously quoted as the "equilibrium end-point." After seven hours the pressure had decreased five millimeters corresponding to propylene polymerization. No further change was noted after twelve hours but about twenty-four hours from the beginning of the reaction the pressure again slowly increased continuing thus for four days to apparent constancy at a value twenty-eight millimeters more than the previous "end-point," thus confirming the belief that the propylene decomposition was responsible for the lack of agreement in the equilibrium studies from the two sides of the reaction. From the experiments the decomposition rate is five times as rapid as the combination reaction, consequently the time of contact of propylene-hydrogen sulphide mixtures must be five times that for the mercaptan thus giving opportunity for considerable propylene decomposition. This does not invalidate, however, the idea that the "end-points" quoted in this paper represent pseudo-equilibrium values since all the reactions showed a constancy for at least two hours; it merely explains why the same "end-points" cannot be reached from the reverse side.

The main steps therefore in the complete mechanism may be represented as follows:

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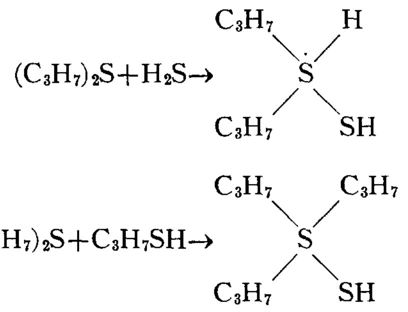
[8] Duffey, Snow and Keyes, Paper presented at the Washington meeting of the Am. Chem. Soc. March, 1933.

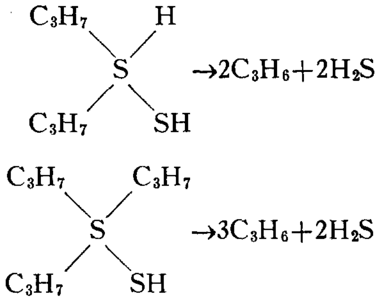
[9] Wheeler and Wood, J. Chem. Soc. 1819 (1930).

Step I $2C_3H_7SH \rightarrow (C_3H_7)_2S + H_2S$



Step II $(C_3H_7)_2S + H_2S \rightarrow \begin{matrix} C_3H_7 & & H \\ & S & \\ C_3H_7 & & SH \end{matrix}$

and $(C_3H_7)_2S + C_3H_7SH \rightarrow \begin{matrix} C_3H_7 & & C_3H_7 \\ & S & \\ C_3H_7 & & SH \end{matrix}$



Step III $\begin{matrix} C_3H_7 & & H \\ & S & \\ C_3H_7 & & SH \end{matrix} \rightarrow 2C_3H_6 + 2H_2S$

and $\begin{matrix} C_3H_7 & & C_3H_7 \\ & S & \\ C_3H_7 & & SH \end{matrix} \rightarrow 3C_3H_6 + 2H_2S$

Step IV $C_3H_6 + H_2S \rightleftarrows (CH_3)_2CHSH$

Step V $C_3H_6 \rightarrow$ polymerization $\rightarrow$ decomposition.

The mathematical difficulties in the solution of the differential equations for the kinetics of such a complex series of reactions prevent elucidation of individual rate constants. It may be noted, however, that Step III must be very considerably faster than either I or II, that Step I mainly controls the length of the induction period and that Step II controls that portion of the reaction arising at the point of inflection.