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Nelson R. Trenner and H. Austin Taylor

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The Thermal Decomposition of Ethyl Mercaptan and Ethyl Sulphide

NELSON R. TRENNER¹ AND H. AUSTIN TAYLOR, *New York University*

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The thermal decompositions of ethyl mercaptan and ethyl sulphide have been studied by a static method and shown to proceed homogeneously in glass vessels which have become poisoned by products of reaction. The rate curves of both exhibit an induction period shown to be due to a reaction between ethyl and hydrogen sulphides yielding what appears to be a dimercaptan. The subsequent decomposition of this intermediate is unimolecular but complicated by a reverse reaction. The energies of activation of formation and decomposition of the intermediate

are each about 40,000 calories, the rate of formation being slightly greater than the rate of decomposition at temperatures around 400°C. The unimolecular rate falls off below 150 mm which would correspond with six squared terms involved in the activation. No foreign gas has been found to maintain the rate. The existence of a complex equilibrium detracts somewhat from the certainty of interpretation of data and mechanism. A critique of similar recent work substantiates the conclusions here drawn though differing from previous interpretations.

THE paucity of accurate data on organic sulphur compounds would alone justify the present study, but in addition the constant literature references to the analogies existing between these sulphur compounds and the corresponding oxygen derivatives, would suggest a simplicity of decomposition mechanism which might be useful at the present time in its bearing on the kinetics of reaction in general. It has frequently been suggested² that the aliphatic mercaptans behave thermally in a manner similar to the amines and might therefore be suspected of decomposing in a unimolecular manner. In fact this is the supposed finding of Malisoff and Marks recently for propyl, butyl, amyl and heptyl mercaptans, both iso and normal. That the sulphur compounds should differ from their oxygen and nitrogen analogs due to the relative ease with which they may be converted from one valence type to another seems to have been continually overlooked. Partly on this account and partly also on account of the methods employed which have usually been dynamic in character, the earlier conclusions regarding the mechanism of mercaptan decomposition are erroneous. This paper will show that the reaction is far from being a simple disruption into hydrogen sulphide and an unsaturated hydrocarbon but in-

volves a series of consecutive reactions, one of which appears to be unimolecular, complicated by the existence of an equilibrium in which polysulphides seem to play an important part. That the reaction is not simple was immediately shown by the first static determination, in the existence of an induction period in the decomposition rate and only by elucidating the cause of this induction period was the mechanism of the whole reaction realized. The study of this induction period called for an investigation of the kinetics of decomposition of ethyl sulphide. The similarity of mechanism found for the thioether and thioalcohol decompositions necessitates their simultaneous discussion and serves further to differentiate between the sulphur and oxygen analogs. This discussion will be facilitated by a presentation of the experimental data for both compounds beforehand.

ETHYL MERCAPTAN

The experimental procedure for all the static studies made was identical with that previously described in reports from this laboratory.³ The mercaptan, initially an Eastman sample, was dried for a week over sodium carbonate, fractionated between 34.8° and 35.5°C and refractionated between 35.0° and 35.3°C. This was then sealed under its own vapor pressure to the reaction vessel-manometer system. The rate of change of

¹ Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June 1932.

² W. F. Faragher, J. C. Morrell and S. Comay, *Ind. Eng. Chem.* **20**, 527 (1928); W. M. Malisoff and E. M. Marks, *ibid.* **23**, 1114 (1931).

³ H. A. Taylor, *J. Phys. Chem.* **34**, 2761 (1930) et seq.

pressure with time could then be followed on the mercury manometer in the usual manner.

A few preliminary experiments showed that the course of reaction involved an induction period with an autoaccelerating rate up to a maximum and a subsequent falling off yielding the hysteresis type curves as shown later. It was early ob-

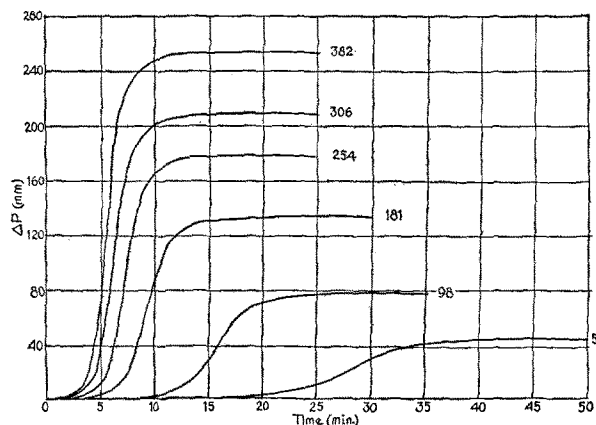


FIG. 1. Curves of the decrease in pressure plotted against time, showing the induction period in the decomposition of ethyl mercaptan at pressures of 51, 98, 181, 254, 306 and 382 mm and at 410°C.

served that although the shape of the rate curve subsequent to the point of inflection was easily reproducible the length of the induction period was quite erratic. It was found however that after three or four experiments had been performed successively the surface of the vessel had become stabilized and results could be duplicated, a duplication which was possible even after some months and in a different reaction chamber. This surface effect is discussed later but necessitated in the work a daily stabilizing of the reaction vessel before reliable results could be obtained.

In this manner data were obtained at temperatures from 380°–410°C and at pressures from 50 to 400 mm. Fig. 1 shows a typical set of curves obtained at 410°C. The peculiar behavior of the induction period suggesting a heterogeneous reaction, a rigorous test was made by adding powdered Pyrex glass to the reaction vessel. The first run made after this addition and complete evacuation of the system gave a decomposition rate for the mercaptan with a greatly reduced induction period. In subsequent reactions the period lengthened until eventually the "stable-

period" with the empty bulb was reproduced. The fact of an induction period, significant as it so frequently is of chain reactions, suggested a further test for homogeneity by the use of a potassium chloride surface. To this end the surface of the empty reaction bulb was coated with the crystalline salt and the rate of decomposition again measured. Results similar to those with the added glass powder were obtained, the induction period being short initially but lengthening with "ageing" to what may be termed the normal in view of its reproducibility. Fig. 2 shows some of the rate curves obtained with added surface and with potassium chloride, the changing length of the induction period being obvious. It will be observed from these curves, as has been found continuously throughout the work, that at a given temperature and given initial pressure the slope of the curve at the inflection is always the same regardless of the length of the induction period. This constancy must mean that if more than one reaction is involved, the secondary ones are strictly homogeneous under all conditions whilst the primary reaction responsible for the induction period though capable of catalysis by the glass surface becomes eventually homogene-

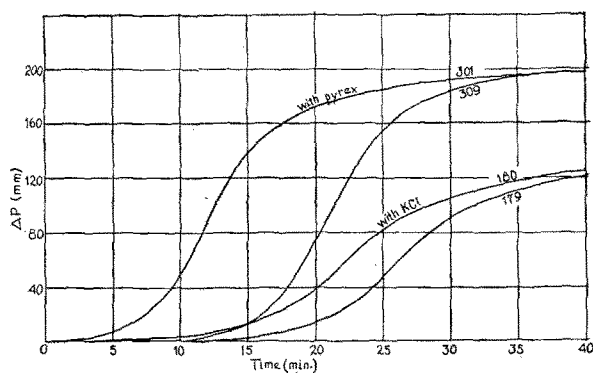


FIG. 2. Rate curves showing the effects of the addition of powdered Pyrex glass (with Pyrex) and potassium chloride (with KCl) to the reaction vessel and two rate curves when no powdered material was added.

ous, possibly through a poisoning of the surface by decomposition products. An inspection of the apparatus showed that the cool connecting tubes to the reaction vessel were gradually darkened by a dark brown or black deposit which would distil off in vacuo on warming, while the reaction vessel kept constantly heated became only slightly

darkened. The deposit is certainly not carbon and in all probability is a polysulphide.

On studying the rate curves obtained for different initial pressures at a given temperature, it appeared that the portion of the curves subsequent to the induction period might well represent a unimolecular reaction. The effect of foreign gases was therefore determined. Ten gases including oxygen, nitrogen, hydrogen, carbon dioxide, propylene, ethylene, sulphur dioxide, helium, hydrogen sulphide and ammonia were used with results shown graphically in Fig. 3. In each case, oxygen excepted, 100 mm of the gas was added to 180 mm of the mercaptan vapor. With oxygen only 5 mm were used because of the pronounced effect it had on the induction period. The significance of the order, relative position and slopes of these curves should be noted. Their importance will appear in the later discussion. For the present suffice to note that the secondary portions of the curves all have the same slope, with the exceptions of propylene and ethylene, substantiating the previously suggested unimolecular character of the later reaction.

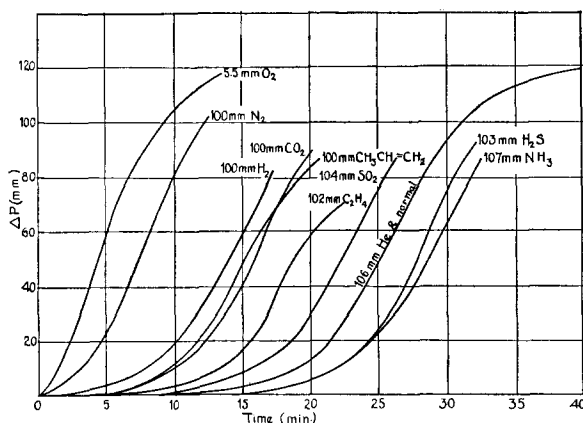


FIG. 3. Rate curves for the decomposition of ethyl mercaptan in the presence of inert gases.

The specific effects of decomposition products were studied by several injection tests made by allowing a certain amount of mercaptan to react until it had reached its maximum rate, that is, the inflection in the rate curve, and then introducing about an equal quantity of fresh reactant whence the rate was followed to the end. Fig. 4 shows the results so obtained in one case. Knowing from previous experiment the shape of the

rate curve for the initial sample, had no injection been made (dotted in the diagram and labelled 'normal'), the rate curve for the injected sample may be 'synthesized' as shown by subtraction of the ordinates of the normal curve from those of the 'actual' observed curve. The curve so obtained will be discussed later.

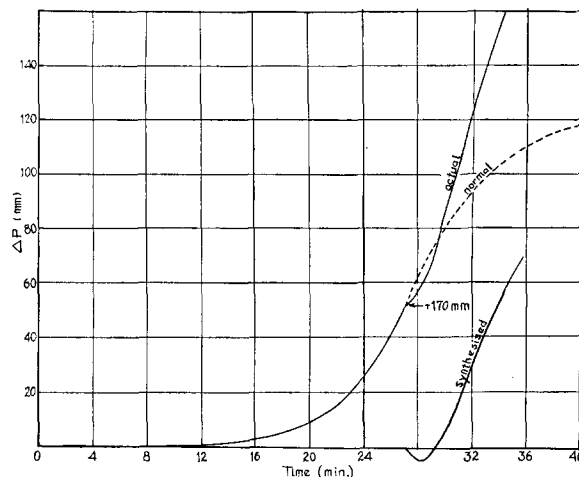


FIG. 4. Rate curve for the decomposition of ethyl mercaptan when an additional sample was added during the course of the experiment. The "normal" curve shows the rate expected, if no addition had been made. The "synthesized" curve is secured by subtracting the ordinates of the "normal" curve from those of the "actual" curve.

The extent of reaction is found to vary with temperature and pressure, a volume increase of from 63 to 76 percent being obtained under varying conditions. That this may represent an equilibrium is qualitatively substantiated by the fact that a higher initial pressure of mercaptan always results in a lower percentage conversion as may be expected for a reaction occurring with a volume increase. Further, a rough calculation from the meagre available data, assuming ethylene and hydrogen sulphide as the final products, shows the decomposition to be endothermal in accord with the observation of a higher percentage conversion at the higher temperatures. As final evidence of an equilibrium, a mixture of 180 mm of ethylene and 190 mm of hydrogen sulphide showed a contraction of 34 percent after twenty-two hours, the reaction appearing to be complete. Such a mixture would correspond to 180 mm of ethyl mercaptan which at the same temperature gave a percentage change of 69.6. With due al-

TABLE I.

| Initial press. in mm | Percent decomp. | t_{25} | t_{50} in min. | t_{75} |
|-------------------------|--------------------|----------|---------------------|----------|
| Temperature 386°C | | | | |
| 380 | 63.3 | 1.54 | 3.12 | 5.99 |
| 309 | 64.6 | 1.57 | 3.34 | 6.46 |
| 254 | 66.5 | 1.49 | 3.31 | 6.24 |
| 180 | 69.6 | 1.80 | 3.60 | 6.89 |
| 99 | 76.4 | 2.98 | 5.97 | 8.67 |
| Temperature 393°C | | | | |
| 383 | 64.0 | 1.05 | 2.20 | 4.03 |
| 311 | 65.5 | 1.20 | 2.53 | 4.69 |
| 254 | 67.5 | 1.16 | 2.38 | 4.60 |
| Temperature 400°C | | | | |
| 383 | 65.0 | 0.76 | 1.61 | 3.00 |
| 311 | 67.2 | 0.77 | 1.64 | 3.25 |
| 252 | 69.0 | 0.84 | 1.74 | 3.25 |
| 181 | 72.2 | 0.81 | 1.88 | 3.60 |
| 99 | 77.1 | 1.16 | 2.36 | 4.32 |
| Temperature 410°C | | | | |
| 382 | 66.2 | 0.57 | 1.10 | 1.94 |
| 306 | 68.2 | 0.54 | 1.12 | 2.06 |
| 255 | 70.0 | 0.58 | 1.14 | 2.03 |
| 181 | 73.4 | 0.54 | 1.11 | 2.15 |
| 99 | 78.8 | 0.58 | 1.47 | 2.60 |
| 51 | 84.0 | 1.10 | 2.13 | 3.86 |

lowance for side reactions as evidenced by the presence of polysulphide these figures are in excellent agreement and significant of an equilibrium in the system. That the later portion of the curve corresponds approximately to a unimolecular reaction may be seen from the values of the quarter, half and three-quarter lives given in Table I. The method of calculating these must be deferred until the mechanism has been presented.

TABLE II.

| Temp. | Init. press. P | Inflection Point | | Press. unreacted P_I | Ratio P_I/P |
|-------|---------------------|------------------|--------|---------------------------|------------------|
| | | Time | Press. | | |
| 386°C | 380 | 17.22 | 84 | 296 | 0.770 |
| | 309 | 20.22 | 78 | 231 | 0.753 |
| | 254 | 22.35 | 72 | 182 | 0.730 |
| | 180 | 25.42 | 52 | 128 | 0.762 |
| 393 | 383 | 13.02 | 90 | 293 | 0.765 |
| | 311 | 14.70 | 78 | 233 | 0.758 |
| | 254 | 16.00 | 67 | 187 | 0.750 |
| 400 | 383 | 9.13 | 93 | 290 | 0.758 |
| | 311 | 10.13 | 79 | 235 | 0.754 |
| | 252 | 11.30 | 62 | 190 | 0.768 |
| | 180 | 13.95 | 58 | 123 | 0.712 |
| 410 | 382 | 5.05 | 90 | 292 | 0.764 |
| | 306 | 5.70 | 78 | 228 | 0.754 |
| | 255 | 6.80 | 72 | 183 | 0.734 |
| | 181 | 9.00 | 57 | 124 | 0.716 |
| | 99 | 15.59 | 34 | 65 | 0.711 |

At the higher pressures the constancy of the quarter lives is good, while at the lower pressures the time increases. There is a marked drift in the times of 75 percent change which may be due to the fact that the reverse reaction causing the equilibrium has not been fully allowed for. Taking mean values of the quarter lives at the higher pressures the Arrhenius equation yields for the energy of activation a value of 40,100 cal. A similar calculation by using the half-lives gives 41,200 cal.

All the above calculations, as will appear later, are made with reference to the later portion of the rate curve that is after the point of inflection. Attempts to separate the several reactions suspected as occurring by a shift of temperature and pressure proved fruitless since it was found that not only is the temperature coefficient of the induction period and hence of the reaction causing it of the same order as that of the subsequent reaction given above but also the ratio of the amount of reactant undecomposed at the point of inflection to the initial pressure is constant with varying temperature and pressure. Table II will illustrate these facts. Furthermore the energy of activation calculated for the induction period alone is 42,800 cal.

ETHYL SULPHIDE

In numerous instances experimenters have found that pyrolysis of a mercaptan yields the corresponding sulphide as one of the products. Thus Kahn⁴ states that octyl mercaptan boiling at 198–200°C decomposes to give octyl sulphide and hydrogen sulphide. For heterogeneous mercaptan decompositions on metallic or metal sulphide surfaces Elgin⁵ and Sabatier and Maihle⁶ found sulphide formation. If this were the general procedure one could easily account for the induction period in the mercaptan decomposition since the formation of a molecule of ethyl sulphide together with a molecule of hydrogen sulphide from two molecules of mercaptan would involve no volume change. The observed volume increase might be due to subsequent decomposition of the ethyl sulphide into ethylene and more hydrogen sulphide. For this to be satisfactory however

⁴ Kahn, Bull. Soc. Chim. Roumania 5, 70 (1923).

⁵ J. C. Elgin, Ind. Eng. Chem. 22, 1290 (1930).

⁶ Maihle, Comptes Rendus 150, 1569 (1910).

ethyl sulphide should show no induction period on decomposition. It was originally in an effort to test this that the ethyl sulphide study was made.

The ethyl sulphide used was an Eastman sample dried over sodium hydroxide and twice fractionated, the fraction employed boiling between 90.8 and 91.6°C at 765.7 mm pressure. The apparatus used was the same as for the mercaptan save that to prevent condensation of the sulphide the capillary tubes outside the furnace were maintained at 100°C by auxiliary heaters. The course of the reaction however contrary to the suggested expectation did involve an induction period and seemed to parallel in almost every detail the mercaptan results suggesting a similarity of mechanism for both decompositions. This similarity was reflected in the effects of increased surface and of added gases as also in the existence of an equilibrium.

The effect of increased surface was precisely as found for the mercaptan, namely, a shortened induction period initially, gradually lengthening to the normal rate as in the empty reaction vessel. As regards the equilibrium, assuming one mole of the thioether to give two of ethylene and one of hydrogen sulphide, there should be a 200 percent change observed. Actually only 112 to 124 percent under varying conditions was found indicating a reaction from 55 to 62 percent complete. These values are considerably lower than for mercaptan but should not be unexpected if an equilibrium exists, in view of the higher ethylene concentration from the thioether as compared with that from mercaptan. As confirmation of this 357 mm of ethylene and 182 mm of hydrogen sulphide were allowed to react at 420°C, and on completion of reaction after twenty-two hours had contracted 24 percent. This, calculated as an equivalent amount of thioether decomposing would correspond to 63.3 percent while the actual observed change for 181 mm of thioether was 62.2 percent, an obvious agreement. Finally with reference to the foreign gases, with one exception, hydrogen sulphide, their effects on the sulphide were precisely similar to those on the mercaptan. With hydrogen sulphide, whereas the induction period of the mercaptan was actually increased, that of the thioether was almost completely removed. It seemed probable that the two reacted together rapidly to yield a product which under-

TABLE III.

| Init. press. (mm) | Percent decomp. | t_{25} | t_{50} (mins.) | t_{75} |
|----------------------|--------------------|----------|---------------------|----------|
| Temperature 393°C | | | | |
| 303 | 56.0 | 1.76 | 3.83 | 7.29 |
| 246 | 57.9 | 1.87 | 4.00 | 7.48 |
| Temperature 400°C | | | | |
| 304 | 57.3 | 1.34 | 2.76 | 5.21 |
| 253 | 57.6 | 1.35 | 2.94 | 5.50 |
| 180 | 61.9 | 1.69 | 3.64 | 6.75 |
| Temperature 410°C | | | | |
| 301 | 58.0 | 0.84 | 1.76 | 3.16 |
| 251 | 59.1 | 0.91 | 1.94 | 3.50 |
| 178 | 61.1 | 0.95 | 2.09 | 3.86 |
| Temperature 420°C | | | | |
| 301 | 59.1 | 0.54 | 1.10 | 1.90 |
| 263 | 59.6 | 0.49 | 1.13 | 2.06 |
| 181 | 62.0 | 0.63 | 1.35 | 2.50 |

went a steady decomposition thereby removing the induction period. This system therefore was made the subject of a special study as is seen later.

Tables III and IV give the salient data for the thioether paralleling those for mercaptan.

The data in Table III are as in the mercaptan case relative to the rates after the induction period. The constancy of quarter lives is again evident, the values yielding an energy of activation of 43,800 calories. The half lives give 42,700 calories whilst the induction period itself gives 43,000 calories. The ratios in Table IV are again seen to be constant although the value is higher than for mercaptan. This is due no doubt to the slightly longer induction period for thioether than for mercaptan. The succeeding rate for thioether is also less than for mercaptan as might be anticipated, the higher ethylene concentration acceler-

TABLE IV.

| Temp. | Init. press. P | Inflec. press. | Press. un- reacted P_I | Ratio P_I/P |
|-------|---------------------|-------------------|-----------------------------|------------------|
| 393 | 303 | 46 | 257 | 0.848 |
| | 246 | 39 | 210 | 0.854 |
| | 183 | 34 | 149 | 0.814 |
| 400 | 304 | 48 | 256 | 0.846 |
| | 253 | 43 | 210 | 0.830 |
| | 180 | 33 | 147 | 0.816 |
| 410 | 301 | 46 | 255 | 0.848 |
| | 251 | 40 | 211 | 0.840 |
| | 178 | 38 | 141 | 0.792 |
| 420 | 301 | 50 | 257 | 0.834 |
| | 263 | 46 | 217 | 0.826 |
| | 181 | 40 | 141 | 0.780 |

ating the reverse reaction indicated by the percentage decompositions shown in Table III. This constancy of the amount decomposed at the point of inflection with varying temperature and pressure again precludes the possibility of separating the reaction into its constituents.

ETHYL SULPHIDE AND HYDROGEN SULPHIDE

The behavior of this system as already mentioned was suggestive that the primary reaction with the ethyl sulphide alone is enormously accelerated in presence of hydrogen sulphide, an acceleration which since it did not occur with the mercaptan is probably due therefore to specific chemical reaction between the ethyl and hydrogen sulphides. It seemed possible that this reaction might be giving rise to a compound which was actually the intermediate, decomposing unimolecularly in both the mercaptan and sulphide cases. If this is true then a study of the velocity and energy of activation should give results in substantial agreement with those already found for the secondary reactions, subsequent that is, to the induction period.

In the experiments made, equivalent quantities of the ethyl and hydrogen sulphides were used. Fig. 5 illustrates the course of the reaction at 386°C the lowest temperature studied.

The induction period has almost entirely disappeared. Even in the worst case at 127 mm a slight induction may be seen but amounts to no more than one minute as compared with the twenty minutes for thioether alone. Added hydrogen even when present in an amount three times

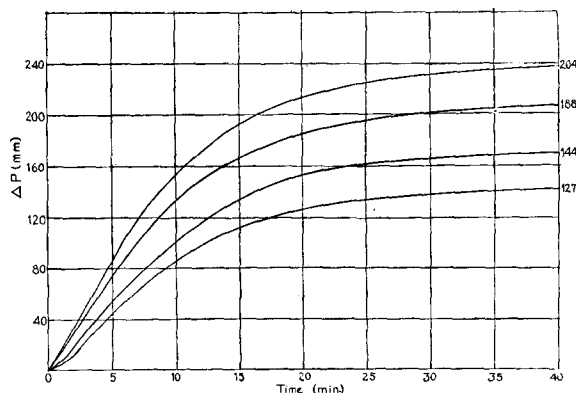


FIG. 5. Rate curves for the decomposition of ethyl sulphide in the presence of hydrogen sulphide.

TABLE V.

| Init. press. | Percent decomp. | t_{25} | t_{50} |
|-------------------|-----------------|----------|----------|
| Temperature 386°C | | | |
| 402 | 59.4 | 3.00 | 6.53 |
| 355 | 60.0 | 3.00 | 6.75 |
| 291 | 60.3 | 3.24 | 7.16 |
| 252 | 58.8 | 3.24 | 7.25 |
| Temperature 393°C | | | |
| 399 | 57.9 | 2.07 | 4.52 |
| 353 | 59.4 | 2.25 | 4.95 |
| 305 | 60.5 | 2.50 | 5.20 |
| Temperature 410°C | | | |
| 402 | 58.4 | 0.98 | 2.08 |
| 350 | 59.3 | 1.07 | 2.30 |
| 309 | 61.8 | 1.06 | 2.39 |
| 252 | 60.6 | 1.16 | 2.58 |

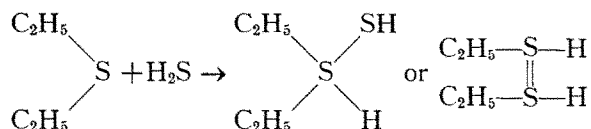
the total reactants was found to be without effect, irrespective also of the initial pressure of reactant. The same was found true of air although here a slight shift of end point was observed possibly due to some oxidation.

In Table V are given the values of the fractional lives showing a constancy indicative of a unimolecular rate. The percentage decompositions are included for comparison. At a pressure of about 300 mm at 410°C the mercaptan changes by 68.2 percent, the ethyl sulphide-hydrogen sulphide by 60.4 (calculated from 150 mm of each) and the pure ethyl sulphide by 57.8 percent. The order of these results clearly indicates the influence of excess of either hydrogen sulphide or of ethylene. The energy of activation calculated from the above data gives an average value of 39,500 calories in good agreement with the value of 40,500 found for the mercaptan.

DISCUSSION OF MECHANISM

The presence of the induction period in the decomposition rate of both the mercaptan and sulphide is to be taken as suggesting the formation of some intermediate, either with no volume change or with a volume decrease, which subsequently decomposes with a volume increase. From the constancy of the energies of activation of both the induction periods and the subsequent rates, from the similar influence of inert gases and lastly from the constant characteristics of the observed end points it is probable that the same intermediate is formed in both cases. Since this induction period for the sulphide is removed in

presence of hydrogen sulphide the intermediate would appear to be formed from them in some such way as:



Subsequent decomposition of this latter into ethylene and hydrogen sulphide would yield the observed overall volume increase. The formation of polysulphides which are actually found might be accounted for by a decomposition of the intermediate into disulphide. Unpublished work in this laboratory shows that the disulphides are much less stable than mercaptan or thioether and furthermore are capable of combining with free sulphur to give polysulphides.⁷ The decomposition of the mercaptan would entail therefore a primary split into sulphide and hydrogen sulphide which would react together as above, accounting for the absence of effect of added hydrogen sulphide on the induction period of the mercaptan since sufficient hydrogen sulphide is already present from the primary reaction.

In confirmation of this suggestion for the intermediate it may be noted that addition reactions to alkyl sulphides are well known. In particular Moelwyn-Hughes⁸ attempting to show that the unimolecular decomposition of triethyl-sulphonium bromide in solution would parallel that in the gas phase, points out that the energy of activation of the combination of ethyl sulphide and ethyl bromide varies from 39,600 to 43,400 calories depending on the solution. The activation energy of the induction period of ethyl sulphide is here found as 43,000 calories an agreement which may well be expected since essentially the same types of bonds are involved in both cases.

If this mechanism be accepted, the secondary

⁷ 10 g of sulphur were sealed with 15 g ethyl disulphide in a tube and heated for 24 hours at 135°C. The sulphur went into solution but failed to precipitate on cooling. The orange colored liquid formed, boiled over a range from 140° to 195°C with no definite halts and left an almost black residue. A check with pure disulphide alone after similar heating boiled over a range of only 149.5–150.5°C.

⁸ E. A. Moelwyn-Hughes, Chem. Reviews 10, 248 (1932).

reactions, subsequent that is, to the induction period and previously spoken of as being unimolecular, should correspond with the decomposition of the intermediate. The actual velocity constants of these secondary reactions in both mercaptan and sulphide cases should agree with those for the ethyl sulphide-hydrogen sulphide reaction. It has been shown in Tables II and IV that the ratio of the amount decomposed at the point of inflection to the amount initially present is constant with varying temperature and pressure for both the mercaptan and the sulphide. This constancy is not impaired by the presence of those gases which may truly be considered as inert as Table VI will show, where values of the ratio are given for mercaptan in presence of various gases at 386°C. It should be noted in the

TABLE VI.

| Added gas | Init. press. P | Inflection point | | Press. unreacted P_I | Ratio P_I/P |
|-------------------------------|------------------|------------------|--------|------------------------|---------------|
| | | Time | Press. | | |
| None | 180 | 25.4 | 52 | 128 | 0.762 |
| N ₂ | 198 | 6.95 | 44 | 154 | 0.778 |
| H ₂ | 181 | 13.4 | 44 | 137 | 0.757 |
| C ₃ H ₆ | 182 | 13.8 | 35 | 147 | 0.808 |
| CO ₂ | 184 | 15.5 | 46 | 138 | 0.750 |
| C ₂ H ₄ | 179 | 16.5 | 27 | 152 | 0.850 |
| SO ₂ | 174 | 21.8 | 44 | 130 | 0.747 |
| He | 178 | 24.8 | 46 | 132 | 0.742 |
| H ₂ S | 188 | 27.4 | 45 | 143 | 0.760 |
| NH ₃ | 186 | 28.5 | 47 | 139 | 0.748 |

above that the nitrogen employed was later shown to be impure, containing oxygen which as was found had an enormous influence on the reaction rate probably due⁹ to the formation of disulphide. Further, ethylene and similarly propylene, being a reactant yields a ratio which is high but which is closely approximate to the value found in the thioether runs.

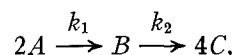
This constancy clearly demonstrates that the temperature coefficient of the reactions before and after the point of inflection must be essentially the same, that the overall rate up to the point of inflection is approximately proportional to the initial pressure and that the concentration of intermediate at the inflection point is independent of the length of the induction period for the same temperature and pressure. In other

⁹ Schmidt's Organic Chemistry, 1st Ed., p. 122 (1927). Beilstein, 4th Ed., 1, 347 (1918).

words the points of inflection on any of the rate curves are comparable points and fractional lives and velocity constants may be calculated from these as a zero time. It is in this way that the previously quoted values were obtained. A further correction has been applied since the end-points at the various temperatures and pressures are variable. In the absence of an exact knowledge of the equilibrium or the actual velocities of the reverse reactions, the end-point of the reaction at the highest pressure for any temperature was taken as a standard and all others compared with it by multiplying their fractional lives by the ratio of the high to low pressure end-points. The correction is not precise but since the change involved is small in any case it was not deemed necessary to elaborate it. The location of the point of inflection was obtained from large plots of the reaction rate curves. On this basis velocity constants were calculated for the secondary reaction, the unimolecular rate, for both the mercaptan and thioether. In Table VII are included for comparison velocity constants for the thioether-hydrogen sulphide reaction calculated directly from observed data. Examination of the

of intermediate, since true constancy is invariably reached only after the first minute and a half after the inflection point. At this point of constancy of the velocity constants then the concentration of the intermediate is at least approximately known and should permit the evaluation of the rate of the primary reaction.

Consider the following scheme:



which could represent equivalent amounts of thioether and hydrogen sulphide combining to give the intermediate which then decomposes into ethylene and hydrogen sulphide. Starting with a mols of A and leaving x mols remaining after time t the rate of disappearance of A is given by $-dx/dt = k_1 x^2$ or $x = a/(1 + ak_1 t)$. Letting $\alpha = k_1/k_2$, $x = a/(1 + ak_2 \alpha t)$ or $\alpha = (a - x)/ak_2 t x$. Taking as values of k_2 the velocity constants previously calculated, for x the difference between the initial pressure and the amount reacted up to the inflection point and expressing these in moles per liter the values of α vary only from 21 to 25 for all the data observed for the mercaptan and from 44 to 47 for the thioether. By taking the data for the thioether-hydrogen sulphide system at the lowest temperature and pressure where an induction period, though slight, does exist, a calculation similar to the above gives for α a value of 91. Too much faith cannot be placed in these actual numerical values, suffice that the order of magnitude of all is the same, whence it is concluded that the primary split of the mercaptan or of the thioether and the combination of thioether and hydrogen sulphide occur at rates only slightly faster than the unimolecular decomposition of the intermediate. Since the first reaction involves a pressure decrease while the subsequent unimolecular reaction results in a larger pressure increase, the observed induction period must be due to a slight actual, though unobservable, pressure decrease by the first reaction before the concentration of intermediate is sufficient for the second reaction to become appreciable. An initial pressure decrease is actually found in the injection tests shown in Fig. 4. Now the injection of fresh mercaptan was made at the point of inflection of the rate curve of the initial mercaptan, at

TABLE VII. *Velocity constants at 393°C.*

| Ethyl Mercaptan | | Ethyl Sulphide-Hydrogen Sulphide | | Ethyl Sulphide | |
|------------------------|-----------------------------|----------------------------------|--------|--------------------------|-------------------------------|
| Init. press. 383 mm | Inflection press. 293 mm | Init. press. 399 mm | | Init. press. 302.5 mm | Inflection press. 255.5 mm |
| Time in mins. | k | Time in mins. | k | Time in mins. | k |
| 0.5 | 0.120 | 1 | 0.0714 | 1 | 0.0359 |
| 1.0 | 0.135 | 2 | 0.0695 | 2 | 0.0364 |
| 1.5 | 0.139 | 3 | 0.0705 | 3 | 0.0376 |
| 2.0 | 0.139 | 4 | 0.0715 | 4 | 0.0385 |
| 3.0 | 0.133 | 5 | 0.0688 | 5 | 0.0392 |
| 4.0 | 0.122 | 6 | 0.0664 | 6 | 0.0401 |
| 5.0 | 0.111 | 7 | 0.0646 | 10 | 0.0440 |
| | | 8 | 0.0627 | | |

constants given as also for those at other temperatures and pressures shows a slight increase for about one and a half minutes, a constancy, and then a falling off. This falling off may be due to the decreased concentration of reactant as in many unimolecular reactions or to complexities caused by the reverse reactions. The preliminary increase appears to suggest that at the point of inflection the primary reactions are not quite complete, but go on building up the concentration

which point, as is shown, the concentration of intermediate is at a maximum. The intermediate, being the result of a bimolecular association, will when formed behave as a quasi-molecule. A stabilization on collision with a mercaptan molecule would result in an increased activation rate for mercaptan and hence an increased rate of formation of intermediate with its resultant pressure decrease.

Turning again to the data in Table I, the values of the fractional lives at all temperatures appear to increase as the pressure falls below 150 mm. If this decrease in rate is truly that to be expected for the deviation of unimolecular reactions with decreasing pressures, an approximate measure of the number of squared terms involved in the activation process may be obtained. The calculation being made in the approximate manner of Hinshelwood¹⁰ gives a value of 6 for the number of squared terms. The inability of added gases, particularly hydrogen, to increase the rate at lower pressures recalls the somewhat similar study on the decomposition of ethylene oxide,¹¹ a reaction also involving an induction period and where the effect of inert gases was somewhat erratic, hydrogen in particular having a marked retarding effect. It is interesting to note that in the mercaptan case the effectiveness with which the various gases reduced the induction period is precisely that found for their effectiveness in quenching mercury fluorescence,¹² which suggests that their action in reducing the induction period may lie in deactivating the nascent intermediate, preventing its dissociation into the original reactants which formed it. Although the necessity for this would not seem great owing to the complexity of the postulated intermediate, the results of the injection tests shown in Fig. 4, where the induction period of the second quantity of mercaptan added was considerably shorter than that of the first, would point in the same direction.

In an endeavor to isolate and study the suspected intermediate several dynamic experiments were made. Since, as has been shown, a maximum

concentration of the intermediate is found in the neighborhood of the point of inflection, the conditions of the dynamics runs were chosen to duplicate these. Ethyl mercaptan vapor was drawn through a tube maintained at a suitable temperature in a furnace, at a rate controlled by a capillary to give a time of contact corresponding to the inflection point in the static experiments. The issuing gases passed through a cooling tube at -15°C , where the tarry materials or higher polysulphides condensed, and thence into a carbon dioxide-toluene freezer where all but the fixed gases were removed. After some time the carbon-dioxide freezer was examined and found to contain a light lemon yellow liquid and a white solid which quickly melted on warming, dissolving in the liquid. Examination showed they were neither ethyl mercaptan nor ethyl sulphide. When washed with sodium hydroxide the liquid went into solution, indicating its acidic properties, and on acidification yielded back the yellow liquid. The liquid had a somewhat pleasant though acroleic penetrating odor. It certainly did not possess any of the characteristically disgusting odors of the mercaptans or sulphides. Efforts to purify it by extraction with ether and vacuum distillation were only partially successful.

A similar procedure with ethyl sulphide gave small amounts of the same yellow liquid along with unchanged sulphide. When hydrogen sulphide and ethyl sulphide were used practically no unchanged ethyl sulphide was found though still only small amounts (less than half a cubic centimeter in eight hours) of the intermediate. This latter fact suggests that the induction period in the thioether is partly due to the necessity of some of it decomposing to give hydrogen sulphide before the intermediate can be formed.

The cause of the small yields of intermediate appears to lie in the fact as previously shown that its rate of formation is only slightly faster than its rate of decomposition. By working at much lower temperatures and high pressure (150 atmos.), sufficient was obtained to allow an analysis to be made. A steel bomb was partly filled with 25 cc ethyl sulphide and 25 cc of liquid hydrogen sulphide in a carbon dioxide freezing bath. The bomb was sealed and raised in temperature to 270°C , being maintained there for 56 hours, a period found to give the best yields without ex-

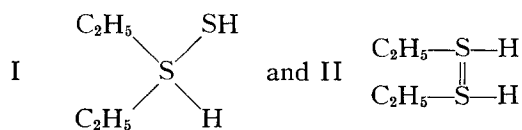
¹⁰ Hinshelwood, *Kinetics of Chemical Change*, p. 126 (1929).

¹¹ W. W. Heckert and E. Mack, Jr., *J. Am. Chem. Soc.* **51**, 2706 (1931).

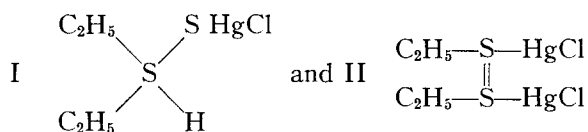
¹² Kistiakowsky, *Photochemical Processes*, p. 126 (1928).

cessive polysulphide formation. The bomb was then cooled in carbon dioxide, opened, allowed to warm up to room temperature removing thereby excess hydrogen sulphide and the remaining light yellow liquid treated with 30 percent caustic soda to separate the mercaptans or intermediate from unreacted sulphide and polysulphides. This solution, after washing with ether to remove mechanically held mother liquor, was then frozen in carbon dioxide and cold dilute sulphuric acid added to liberate again the acid constituents. The necessity for carrying this out in the cold is due to the fact that decomposition of the intermediate is considerably hastened by the presence of an acid, as frequent loss of the product at this stage unfortunately proved. The light yellow liquid was taken up in ether and by addition of mercuric chloride converted into the mercury addition salt which is insoluble in ether and had a light buff color. The yield of the salt was about three grams. The free intermediate could then be obtained by warming the salt in an atmosphere of hydrogen sulphide, forming mercuric sulphide, hydrogen chloride and free intermediate. The sample so obtained was still impure, having a decided mercaptan odor. That it was not mercaptan was shown by its boiling point from 48 to 49.5°C. In fact there seems to be no chemical means of separating this compound from mercaptan.

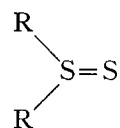
An analysis by the Carius method for sulphur as barium sulphate and chlorine as silver chloride proved totally impossible in presence of the mercuric ion, precipitation of both, especially silver chloride, being incomplete. However by treating the solution from the Carius combustion when only slightly acid with magnesium turnings both silver and mercury may be replaced and the resultant solution analyzed in the usual manner, first for sulphate with barium nitrate and then for chloride with silver nitrate. The mercury analysis is made by weighing mercuric sulphide left after treatment of the mercury salt of the intermediate with hydrogen sulphide at 100°C. The analyses made gave for mercury 69.56, sulphur 11.79 and chlorine 10.88 percent. Taking the earlier suggestions for the intermediate, namely:



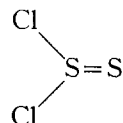
Addition compounds with mercuric chloride would probably yield



Calculated analyses for these two give for I, Hg 55.90, S 18.10 and Cl 9.98 percent, and for II, Hg 67.50, S 10.80 and Cl 11.80 percent. The observed analysis is obviously in better agreement with the second formula, the divergence being undoubtedly due to impurities in the sample obtained. There is however always the possibility that the addition salt in I might also involve two HgCl groups though the second —S—H is hardly a true mercaptan grouping. If this were so, no difference could be noted between the possibilities. It will be observed, too, that the results calculated for case II are precisely those one would obtain for ethyl mercaptan but the intermediate is certainly not mercaptan as judged by its boiling point and other characteristics if not by its odor. In view of the uncertainties on the structure of even the disulphides it seems futile to attempt any further elaboration save to mention the possibility of both. Naik¹³ for example presents evidence for dithioethers of structure

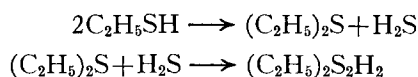


suggesting a dual character for sulphur monochloride as Cl—S—S—Cl or



depending upon the polar conditions.

The following reactions therefore appear to have been established:



As to the subsequent reactions all that may be

¹³ K. G. Naik, J. Chem. Soc. **119**, 379, 1231 (1921).

said is that hydrogen sulphide and ethylene are present in large quantities along with polysulphides. It is difficult to say whether the intermediate breaks up in the main directly into hydrogen sulphide and ethylene with polysulphides as only a secondary reaction, or whether first disulphide and hydrogen are formed, the disulphide rapidly decomposing as we have found into ethylene, hydrogen sulphide and free sulphur from which innumerable possibilities suggest themselves for polysulphide formation. Suffice to say that we have shown that ethylene and hydrogen sulphide will react together on heating to give mercaptan and the intermediate, which under the experimental conditions opens up all the above possibilities, yielding the highly complex equilibrium spoken of throughout the paper.

In conclusion it may be well to consider somewhat briefly the foregoing in comparison with recent similar work, particularly that by Malisoff and Marks,¹⁴ who find no evidence of any intermediary stages in the reaction mechanism. At the outset their assumption that "no drastic extraneous effect was introduced by the presence of solvent vapors" is open to serious question since as here shown inert gases do markedly affect the induction period, and where unsaturated hydrocarbons are present, the subsequent rate is also changed. They do in fact observe this result with benzene and suggest for it a 'promoter action.' Admitting that the higher homologs are slightly less stable the induction period at 425°C in the presence of an inert gas, which tends to reduce it further, must be small, probably less than a minute. An exposure time of 50 seconds, then, would carry well into the subsequent reactions, though for 10 seconds there should be little if any reaction. This is precisely what they find, namely no reaction of amyl mercaptan at 425° after 9 seconds contact time. They speak further of a range sensitive to the time of exposure occurring at about 52 seconds which from the present work would seem to correspond to the point of inflection. Although, therefore, no induction period was mentioned by them, internal evidence would suggest it. With regard to the effect of foreign gases it is hardly surprising that Malisoff and

Marks should find no effect from hydrogen and carbon dioxide since the latter serve only to replace a small amount of the solvent vapors already present to an extent of 6.5 times the reactant.

The absence of any intermediary stages in mercaptan decomposition is judged by Malisoff and Marks from the constancy of the ratio of the amount of mercaptan decomposed to hydrogen sulphide produced. Such a conclusion is hardly justifiable where the intermediate, as has been shown, reacts analytically as a mercaptan. The fact that in the majority of their results the amounts of hydrogen sulphide produced exceed the amounts of mercaptan decomposed indicates serious analytical error as is shown also by their tests for homogeneity where, on an increased surface, a longer contact time gave a smaller percentage decomposition. It is difficult also to understand how with an admitted accuracy of ± 2 percent in mercaptan estimation they state that the mercaptan formed from amylene and hydrogen sulphide was less than 0.001 percent. The temperature coefficient which they find of 1.38 for amyl mercaptan is considerably lower than is found here for the ethyl derivative as also for propyl mercaptan at present under investigation. From their paper this would appear to be due to unjustifiable averaging of numerous erratic results. The parallelism of their temperature coefficient plots is difficult to see and the fact that they are actually straight lines is open to question since but two points are given on each.

In view of these criticisms it would not be justifiable to accept their conclusions that mercaptan decomposition involves a straight split into olefine and hydrogen sulphide in a manner satisfactorily accounted for by a single unimolecular rate.

The main conclusions then to be drawn from the paper are:

1. Decompositions of ethyl mercaptan and ethyl sulphide show a marked parallelism involving the same intermediate and proceeding to the same equilibrium, which is highly complex.
2. The intermediate has been isolated and shows the properties of a mercaptan but with

¹⁴ W. M. Malisoff and E. M. Marks, *Ind. Eng. Chem.* **23**, 1114 (1931).

- physical characteristics that differentiate it from any so far described.
3. The intermediate decomposes unimolecularly with an energy of activation of about 40,000 calories at a rate only slightly less than its rate of formation from ethyl sulphide and hydrogen sulphide.
 4. Analogies between sulphur and oxygen compounds are liable to be erroneous unless due account is taken of the possible multivalence of sulphur. This has been discussed in connection with recent incorrect suggestions on the mechanism of mercaptan decomposition.