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PYROLYSIS OF ETHYL MERCAPTAN[1]

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ABSTRACT

The decomposition of ethyl mercaptan to ethylene and hydrogen sulphide was studied at various temperatures, with and without a catalyst. Metal sulphides (copper, nickel, and cadmium) proved to be the most efficient catalysts for cracking ethyl mercaptan into unsaturated end products, the optimum temperature being 500–600° C. When no catalyst was used a 40–50% yield of ethylene and a nearly quantitative conversion to hydrogen sulphide was observed between 600 and 700° C. Other products identified in the exit gas were carbon disulphide, carbonyl sulphide, methane, hydrogen, ethane, thiophene, diethyl sulphide, and free sulphur. Identification of these products was aided by infrared and mass spectral analysis of the gas. A tentative mechanism for the reaction justifying the presence of the above by-products is outlined.

INTRODUCTION

Sabatier and Mailhe (4) report that diethyl sulphide and hydrogen sulphide are formed when dry ethyl mercaptan is passed over a cadmium sulphide catalyst at 330° C. and that upon heating to 380° C. ethylene and hydrogen sulphide are quantitatively formed:

$$2CH_3CH_2\text{—}SH \xrightarrow[\text{CdS}]{330^\circ\text{ C.}} (CH_3CH_2)_2S + H_2S \qquad [1]$$

$$CH_3CH_2\text{—}SH \xrightarrow[\text{CdS}]{380^\circ\text{ C.}} CH_2{=}CH_2 + H_2S. \qquad [2]$$

The conditions reported by Sabatier and Mailhe were reproduced but no reaction product was obtained. Hydrogen sulphide was absent, which proved that even diethyl sulphide was not formed (Eq. [1]) at this temperature. A study was then undertaken to determine the optimum conditions for the preparation of ethylene and hydrogen sulphide from ethyl mercaptan.

APPARATUS

The reaction chamber consisted of a Pyrex or silica tube 24 in. in length and 1 in. in diameter mounted vertically in a cylindrical furnace. The bottom of the tube was connected through a ground-glass joint to a two-necked flask which served as the vaporization vessel. To the second neck was attached a measuring dropping funnel for the introduction of ethyl mercaptan. The products of the reaction were allowed to escape through an opening at the

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top of the reaction chamber and passed through an upright water-cooled condenser. The gaseous fraction was led from the top of the condenser to a series of scrubbers (for H_2S and unsaturated compounds) while condensable materials were retained in a flask attached to the bottom of the condenser. In operation the reaction tube was packed with alternate layers of glass wool and catalyst, or glass wool only. The inside temperature was recorded by means of a thermocouple. The vaporization flask was heated by a glas-col mantle.

GENERAL METHOD

In operation a weighed quantity of ethyl mercaptan was added from the dropping funnel at the rate of 1 gm. per min. to the vaporization flask which was held at 150°C. The volatilized mercaptan entered the reaction tube (held at a constant temperature) and emerged as a mixture of gases and some condensable products. The gases were bubbled first through water to remove free sulphur, then through 30% sodium hydroxide to remove hydrogen sulphide, and finally through bromine (under water) to remove unsaturated material.

When a total analysis of the reaction products was required a sample was taken directly from the top of the condenser. Using an Orsat apparatus, the sample (100 ml.) was measured at equalized pressure and sent through an absorption pipette containing 30% sodium hydroxide until the volume of remaining gas remained constant. The loss in volume was measured as hydrogen sulphide. Unsaturated materials were removed with fuming sulphuric acid (20%) or bromine. The remaining portion was passed through hot copper oxide several times to determine its hydrogen content, and then the remainder was burned in the presence of oxygen and the volumes of carbon dioxide and water formed were measured. The latter measurements enable one to determine the amount of methane and ethane in a sample of gas when only the two are present.

RESULTS

Since cadmium sulphide was reported as a good catalyst by Sabatier, it was studied over a wide range of temperatures. One mole of ethyl mercaptan was used and samples were taken five to ten minutes after the reaction had begun, to ensure the absence of air.

With this catalyst, formation of ethylene (Table I) started at 400° C. with a yield of only 5.7% of the total gases coming out of the reactor. Also much liquid condensed, which was identified as diethyl sulphide with minor quantities of ethyl mercaptan.

A maximum yield was attained at 600° C. with 24.1% of ethylene in the gas mixture. As can be noted, the ethylene formation passed through a maximum at 600° C. The hydrogen sulphide formation was very high at the start and then decreased steadily with increasing temperatures. Sulphur was also formed in small amounts.

Hydrogen formation increased with the temperature of pyrolysis. This is undoubtedly due to the cracking of hydrocarbon or hydrogen sulphide. Also the mixture of gas B after ethylene, hydrogen sulphide, and hydrogen have

TABLE I

COMPOSITION OF EFFLUENT GASES

Catalyst	Temp., ° C.	C_2H_4, %	H_2S, %	H_2, %	B, %
CdS	300	Nil	Nil	Nil	Nil
	350	Nil	Nil	Nil	Nil
	400	5.7	88.4	Nil	5.9
	450	10.5	75.2	8.5	5.8
	500	16.3	58.7	14.0	11.0
	550	20.3	47.2	17.7	14.8
	600	24.1	44.5	16.9	14.5
	700	17.6	37.4	24.0	21.0
NiS	400	Nil	Nil	Nil	Nil
	450	20.2	64.8	1.0	14.0
	500	28.8	52.1	1.3	17.8
	550	27.0	51.5	1.3	20.2
	600	27.9	48.9	3.2	21.0
	700	26.8	43.0	6.8	23.4
$(Al_2O_3)_x(SiO_2)_y$	400	Nil	Nil	Nil	Nil
	450	29.5	0.5	0.5	2.0
	500	30.3	0.4	0.4	10.0
	550	30.6	0.4	0.4	15.0
	600	25.5	1.3	1.3	21.0
	700	19.6	9.0	9.0	26.0
None	450	Nil	Nil	Nil	Nil
	500	31.9	49.4	0.8	17.9
	550	30.9	49.0	0.9	19.2
	600	29.1	48.5	0.8	21.6
	650	28.1	46.3	2.4	23.2
	700	30.1	45.0	4.1	20.8

B refers to gases that could not be analyzed by the Orsat apparatus.

been removed increased with the temperature. This mixture of gases when burned in the Orsat apparatus could not be calculated as methane and ethane.

Following these results a search for a more efficient catalyst was made. Other sulphides were studied.

With nickel sulphide catalyst (Table I) results were similar to cadmium sulphide except that the formation of ethylene took place at a higher temperature (450° C. instead of 400° C.).

Other sulphides were used, namely those of cobalt, copper, and iron, and gave similar results to nickel sulphide with minor differences.

Aluminosilicate behaved like sulphides, except that less hydrogen was formed. The yield of ethylene was about 30% at 500° C.

Without a catalyst (Table I), ethylene was produced at 500° C. and the composition of the gas remained nearly constant from 500 to 700° C.

IDENTIFICATION OF PRODUCTS

The condensate obtained from the reaction products was quite large at low reaction temperatures. This was shown by a boiling point determination to be diethyl sulphide with a small amount of unreacted ethyl mercaptan.

A white colloidal material was noticed in the water scrubber after the reaction had proceeded for 30 min. Extraction with carbon disulphide removed this material. Upon evaporation sulphur was obtained.

(a) *Infrared Spectra*

The gas coming out of the reactor was sampled in a gas cell with sodium chloride windows. Another sample was usually taken after hydrogen sulphide and ethylene were removed.

Ethylene was easily identified by its broad and very intense band at 949 cm.$^{-1}$ and a triplet at 1860, 1889, 1910 cm.$^{-1}$ (3). Other bands may be common to other products.

After removal of ethylene and hydrogen sulphide, the spectrum also showed the presence of methane with an absorption band at 1306 cm.$^{-1}$ (3) and of ethane at 820 cm.$^{-1}$ (3).

The mixture also contained carbon disulphide as shown by the band at 2183 cm.$^{-1}$ (3).

Carbonyl sulphide was detected by its very intense absorption at 2050 cm.$^{-1}$, which in many cases has a dual nature under dilution (1). Another band which might be characteristic of thiophene was present at 710 cm.$^{-1}$ (2). The spectrum of the unscrubbed and scrubbed gases is fully explained and all bands were assigned to known gases.

(b) *Mass Spectrometry*

In order to know the relative amount of product present in one of these mixtures of gases mass spectral analysis was used. Since the Orsat apparatus could give reasonable accuracy for the estimation of ethylene, hydrogen sulphide, and hydrogen, the samples used for mass spectral analysis were free of hydrogen sulphide and ethylene.

Results obtained when using cadmium sulphide catalyst at 500° C. showed an average composition of 41% of ethane, 8.4% of methane, and 47% of hydrogen, and traces of other materials such as carbon disulphide, carbonyl sulphide, and thiophene. Therefore the proportion of ethane in this gas mixture is high and that of methane, low. The composition of this fraction of gas indicates cracking of ethane or ethylene.

DISCUSSION

The pyrolysis of ethyl mercaptan under flow conditions is very slightly catalytic if at all. With the best catalysts used, such as sulphides of copper, nickel, cobalt, and cadmium, the lowest temperature at which ethylene is produced is 450° C. The yield is small, and the best temperature for the optimum formation of ethylene, with catalysts, is 500° C. Moreover, from 500 to 700° C. without a catalyst, the yield of ethylene is practically constant. It is considered that temperatures of 500–600° C. would be efficient using Pyrex or silica tubes packed with glass wool.

MECHANISM

The basic reaction in the pyrolysis of ethyl mercaptan is analogous to the dehydration of ethyl alcohol. This dehydration reaction is reversible under certain conditions. Also the pyrolysis of ethyl mercaptan, which can be termed as a desulphurization process, is a reversible reaction:

$$CH_3CH_2\text{—}OH \underset{H_2SO_4}{\overset{Al_2O_3}{\rightleftharpoons}} CH_2\text{=}CH_2+H_2O \qquad [3]$$

$$2EtOH \longrightarrow Et_2O+H_2O \qquad [4]$$

$$CH_3CH_3SH \rightleftharpoons CH_2\text{=}CH_2+H_2S\,. \qquad [5]$$

At lower temperatures, when the hydrogen sulphide formation is high, some liquid is formed, which was identified as diethyl sulphide (Eq. [1]).

Since elemental sulphur is formed in the pyrolysis, it should come from the decomposition of hydrogen sulphide which is said to start at 400° C. Even if the dissociation of hydrogen sulphide is small, the equilibrium is shifted to the right by removal of sulphur or hydrogen, which are both present in the reaction products.

Ethane is found at all the temperatures studied as evidenced by the infrared spectra obtained. It is likely to be formed by the reduction of ethylene with the hydrogen generated from hydrogen sulphide. At higher temperatures methane is produced in greater proportion and the hydrogen content of the gaseous products is higher indicating that another pyrolysis is taking place.

Carbon disulphide, carbonyl sulphide, and thiophene are also formed in traces. The occurrence of carbon disulphide indicates that methane has reacted with sulphur vapor (Eq. [6]). This reaction is the basis of a commercial process to make carbon disulphide:

$$CH_4+4S \longrightarrow CS_2+2H_2S\,. \qquad [6]$$

The presence of carbonyl sulphide is due to some oxygen in the system, probably some oxide impurity in the catalyst, and the presence of thiophene is due to the dehydrogenation of diethyl sulphide or to the condensation of ethylene with hydrogen sulphide followed by dehydrogenation.

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