
A thermodynamic investigation of pentanethiol pyrolysis reaction

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The most reliable pentanethiol pyrolysis reaction product formation probabilities were investigated when hydrogen sulfide, lower molecular mass thiols and sulfur were evolved. It was found that up to 850 K the most reliable reaction products were hydrogen sulfide and methane, while above 850 K methane decomposed to carbon and hydrogen.

Key words: thermodynamics, pentanethiol, Gibbs energy, pyrolysis

INTRODUCTION

It is very important to determine what reactions take place when pollutants are emitted into the atmosphere and how to direct these processes in such a direction that a minimum amount of pollution could occur. Among other processes, the heating of sulfur-rich crude oil products causes emissions of the toxic materials, hydrogen sulfide and gaseous thiols, with obnoxious odour. The maximum permissible concentration for hydrogen sulfide in inhabited areas is strictly regulated and should not exceed 0.008 mg/m³. More strict norms are in force for thiols, and the lower the thiol molecular mass, the lower the permissible concentrations; e. g. if butanethiol has a maximum permissible concentration of 0.0003 mg/m³, propanethiol 0.00005, ethanethiol 0.00003 mg/m³, then methanethiol – 0.000009 mg/m³ [1]. These thiol compounds decompose when sulfur-rich crude oil products are pyrolyzed or oxidized in the lack of oxygen.

The use of thermodynamic analysis methods allows us to determine which chemical reactions are the most probable and which reactions can not occur at all [2]. The equilibrium concentrations of reaction products were calculated for a large number of reactions and found to agree very well with the analytical data [3]. The aim of this investigation was to determine the most reliable chemical reactions taking place during the pyrolysis of pentanethiol.

EXPERIMENTAL

The probability of reaction was judged by the Gibbs energy change.

Changes in Gibbs energy values were calculated using the conventional equation:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \quad (1)$$

The standard entropy and the formation enthalpy values of various compounds at various temperatures given in reference [3] were used for this investigation.

RESULTS AND DISCUSSION

The pentanethiol pyrolysis reactions were divided into three groups: 1 – those in which hydrogen sulfide is evolved, 2 – when one of the reaction products is a lower molecular mass thiol, and 3 – when elementary sulfur is liberated.

Reactions when hydrogen sulfide is liberated into the atmosphere

The Gibbs energy changes at various temperatures calculated for pentanethiol pyrolysis reactions when hydrogen sulfide is evolved into the atmosphere are shown in Fig. 1.

As follows from Fig. 1, the most reliable product of chemical reaction between all saturated hydrocarbons (curves 1–4) is methane (curve 4). The value of Gibbs energy change decreases constantly for all these reactions with an increase in temperature, and the lower the molecular mass of evolved saturated hydrocarbon, the lower the Gibbs energy change.

Curves 5–8 depict the chemical reactions during which unsaturated hydrocarbons are evolved. These reactions are not possible below 400 K, because the

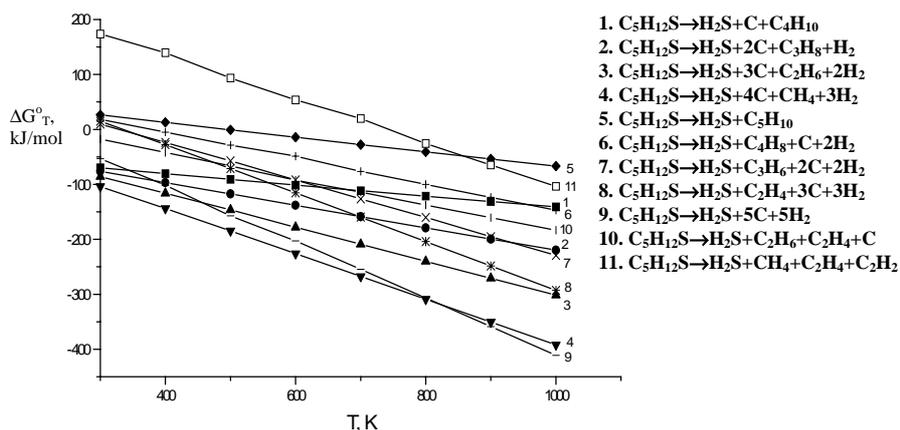


Fig. 1. Gibbs energy dependence on temperature for pentanethiol pyrolysis when hydrogen sulfide is liberated into the atmosphere according to the given reaction equations

Gibbs energy changes are positive. Above 400 K, a similar regularity is correct, especially as saturated hydrocarbons are evolved: the most reliable reaction products are lower molecular mass hydrocarbons. When unsaturated hydrocarbons are liberated the values of Gibbs energy change decrease more steeply with an increase in temperature in comparison with reactions when saturated hydrocarbons are liberated. Therefore, ethylene (curve 8) and propylene (curve 7) liberation at temperatures above 700 K is more reliable than corresponding saturated hydrocarbon products – ethane (curve 3) and propane (curve 2). The value of Gibbs energy change decreases most steeply with an increase in temperature for reactions during which carbon and hydrogen are evolved (curves 6–9). The last of these reactions (curve 9) is the most reliable of all the reactions reviewed here above 800 K.

The product of the last considered chemical reaction is acetylene (curve 11). As is seen in Fig. 1, this reaction is possible only at temperatures above 750 K. However, evolution of acetylene from the reaction at temperatures above 850 K is more reliable than the liberation of pentane (curve 5), because the value of Gibbs energy change for the latter reaction decreases most significantly with an increase in temperature.

Reactions during which lower molecular mass thiols are liberated

These chemical reactions can be described by seven equations. Their values of Gibbs energy change are given in Fig. 2.

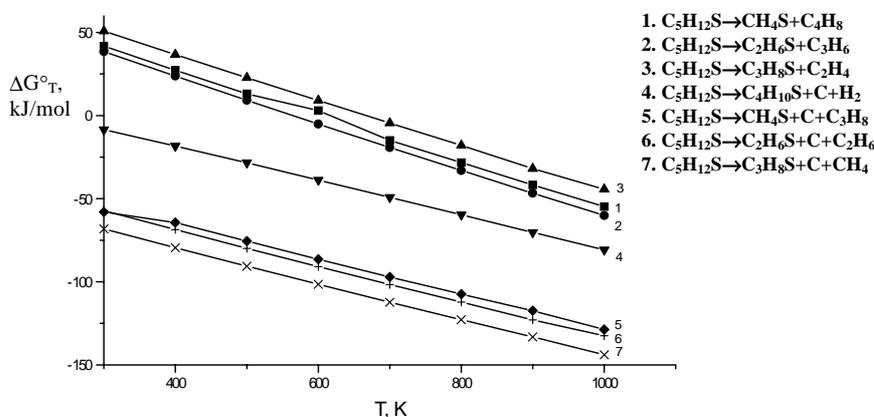


Fig. 2. Gibbs energy changes dependence on temperature for pentanethiol pyrolysis when lower molecular mass thiols are liberated according to the given reaction equations

As one can see from Fig. 2, the Gibbs energy values decrease for all reactions with an increase in temperature. The reactions where unsaturated hydrocarbons (equations 1–3) are liberated are possible only at temperatures above 700 K. On the contrary, chemical reactions when unsaturated hydrocarbons (Fig. 2, equations 5–7) are liberated are possible at all temperatures – these reactions are more reliable than ones that liberate unsaturated hydrocarbons. The fourth reaction is an intermediate one, here carbon and hydrogen are liberated. This chemical reaction is possible at all temperatures, and its reliability also increases with an increase in temperature.

Most reliable is the 7th reaction, during which pentanethiol is converted to propanethiol (or propyl mercaptan) and carbon with liberation of methane. Least reliable is the 3rd chemical reaction, where propanethiol and ethylene are formed. This chemical reaction is possible only at temperatures above 650 K.

Reactions during which elementary sulfur is liberated

One can see in Fig. 3 that the values of Gibbs energy change for all these reactions at all temperatures are negative, with the exception of the 6th reaction where the values of Gibbs energy change are positive when sulfur is liberated in gaseous state.

Also Fig. 3 shows that the absolute values of Gibbs energy change are lower, the higher is the molecular mass of hydrocarbon liberated from pen-

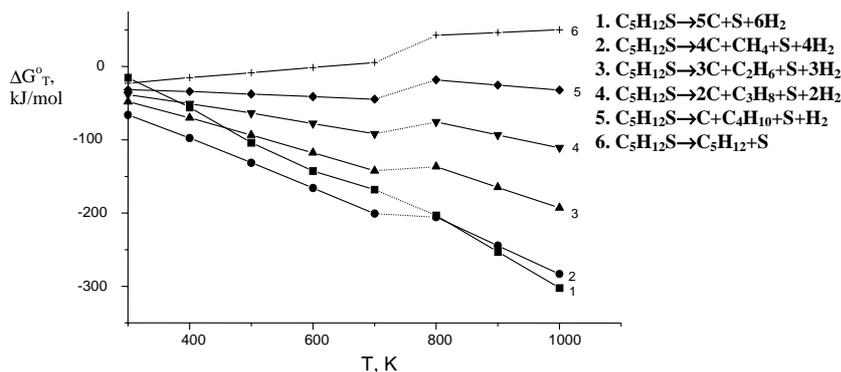


Fig. 3. Gibbs energy dependence on temperature when sulfur is liberated into the atmosphere during pentanethiol pyrolysis according to the given reaction equations

tanethiol molecule at various temperatures (curves 2–6). The sudden break in these curves at 700–800 K is connected with the transformation of sulfur from the liquid state to the gaseous phase.

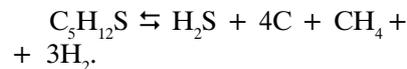
The largest values of Gibbs energy change were observed for the first and second reactions, where methane was evolved or the pentanethiol molecule decomposed to elements. The least reliable reaction was the sixth one. This reaction is thermodynamically impossible at temperatures above 700 K.

Comparison of most reliable pentanethiol pyrolysis reactions

The variation of Gibbs energy changes with temperature for most reliable pentanethiol pyrolysis reactions of all three above-mentioned groups is shown in Fig. 4. One can see that the advantageous pentanethiol pyrolysis reactions are connected with the liberation of hydrogen sulfide (curves 1–3). Less probable reactions are those where sulfur is liberated (curves 6–7). The least probable reactions with decreasing probability are those in which lower molecular mass thiols (curves 4–5) are formed. An increase of Gibbs energy change for pentanethiol decomposition to lower molecular mass thiols can be explained by the fact that it is unstable at higher temperatures. Here, hyd-

rogen sulfide is also one of the decomposition products.

Consequently, the most reliable pentanethiol pyrolysis reaction below 850 K can be expressed by the equation:



Above 850 K the dominating chemical reaction is the one when pentanethiol decomposes to hydrogen sulfide and carbon:

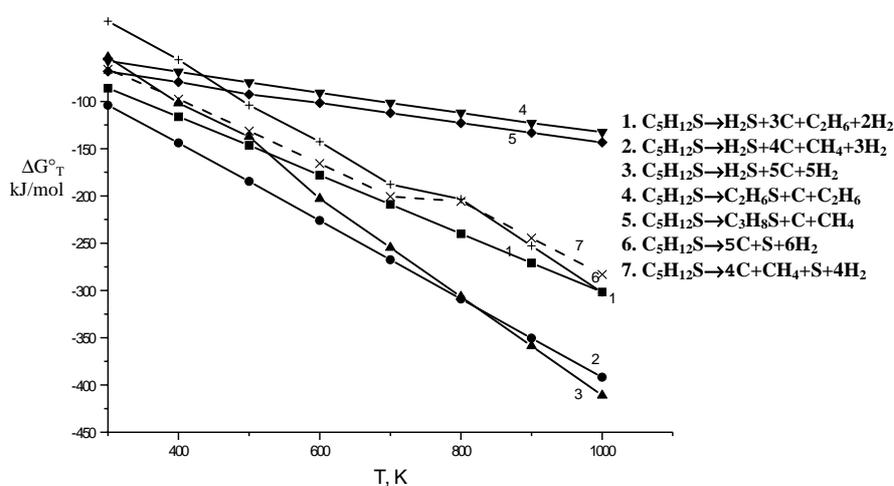


Fig. 4. Temperature-related Gibbs energy changes for the most reliable pentanethiol pyrolysis reactions with liberation of hydrogen sulfide (curves 1–3), lower molecular mass thiols (curves 4, 5) and sulfur (curves 6, 7)

This can be explained by the fact that methane becomes an unstable compound at higher temperatures: it decomposes to hydrogen and carbon (Fig. 5).

Figure 5 shows that the methane decomposition reaction (curve 2) begins to dominate at high

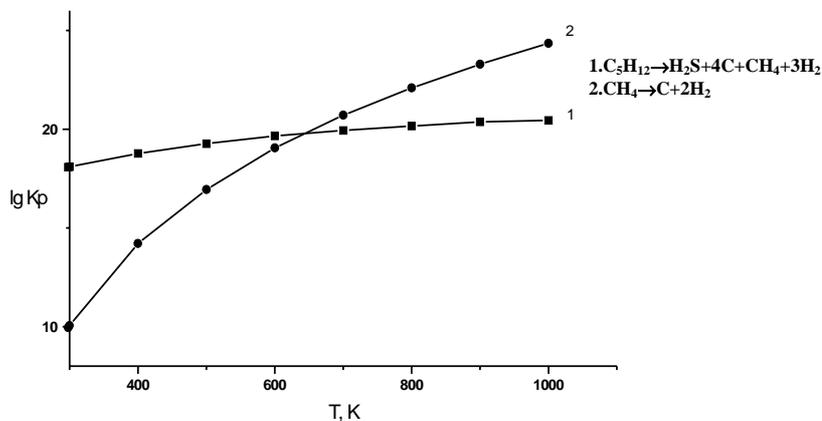


Fig. 5. Pentanethiol and methane pyrolysis equilibrium constant dependence on temperature for reactions according to the given equations

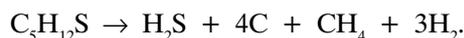
her temperatures, in spite of the fact that the equilibrium constant values for both reactions are expressed by relatively high values.

CONCLUSIONS

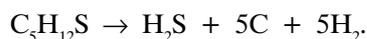
1. The values of Gibbs energy change were calculated for pentanethiol pyrolysis process at various temperatures when hydrogen sulfide, or lower molecular mass thiols, or elementary sulfur are liberated.

2. It has been determined that for pentanethiol pyrolysis process the most reliable sulfur containing reaction product is hydrogen sulfide. Less reliable is elementary sulfur and least reliable are lower molecular mass thiols. The values of Gibbs energy change increase with an increase in temperature during thiol liberation, because the liberating hydrogen sulfide decomposes itself.

3. The most reliable pentanethiol pyrolysis products are methane, hydrogen sulfide, carbon and hydrogen at temperatures up to 850 K. The pyrolysis equation is as follows:



Above 850 K methane decomposes to hydrogen and carbon, and the most reliable reaction at higher temperatures can be described by the equation:



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PENTANTIOLIO PIROLIZĖS REAKCIJŲ TERMODINAMINIAI TYRIMAI

S a n t r a u k a

Apskaičiuotos pentantiolio pirolizės reakcijų Gibso energijos pokyčio vertės įvairiose temperatūrose, kai reakcijos metu išsiskiria sieros vandenilis, mažesnės molekulinės masės tiolis arba siera. Nustatyta, kad patikimiausias sieros turintis reakcijos produktas yra sieros vandenilis, mažiausiai patikimas – mažesnės molekulinės masės tiolis. Nustatyta, kad iki 850 K patikimiausia pentantiolio pirolizė vyksta pagal lygtį



Kadangi aukštesnėse temperatūrose metanas skyla į anglį ir vandenilį, esant daugiau kaip 850 K patikimiausia pentantiolio pirolizės reakcija gali būti aprašyta lygtimi

