

Kinetics of Thermal Decomposition of Thiourea

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Abstract—Thermal decomposition of thiourea in a melt was studied by isothermal and nonisothermal kinetic methods. The influence of the gas flow rate over the melt, layer thickness, and other factors on the process was elucidated. The kinetic parameters of the steps of formation of guanidinium thiocyanate and solid cyclic compounds, products of thiourea thermolysis, were determined.

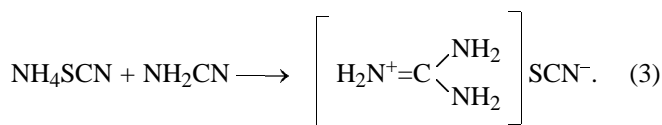
Thermal decomposition of thiourea (Thio) was studied in numerous works [1–4]; their goals were to identify the decomposition products, elucidate the pattern of chemical transformations, and determine the temperature ranges of the main steps.

As the temperature is increased, the following decomposition steps occur.

(1) Isomerization of thiourea into ammonium thiocyanate [reaction (1)], occurring simultaneously with melting of thiourea in the range 140–180°C; the reaction is reversible, and the equilibrium ratio $\text{SC}(\text{NH}_2)_2 : \text{NH}_4\text{SCN} = 1 : 3$ is attained [1, 3, 5].



(2) Formation of guanidinium thiocyanate by reactions (2) and (3) proceeding in the liquid phase above 180°C with the release of a large amount of gaseous products [3].



(3) Pyrolytic decomposition of guanidinium thiocyanate with formation of solid cyclic compounds (melam, melem) in the range 220–300°C.

The kinetics of isomerization of Thio in the solid phase and in a melt was studied in detail by Kharitonov *et al.* [5]. They determined the activation energies of isomerization (kJ mol^{-1}): 157.13 for Thio and 148.82 for ammonium thiocyanate.

In this work we studied the kinetics of the second

and third steps of thermal decomposition of Thio by the methods of isothermal and nonisothermal kinetics.

We found no data on how the heating rate and sample weight affect the thermal properties of a Thio melt. The heating curves obtained at various linear heating rates β (Fig. 1) show that the thermolysis mechanism is independent on whether the process is performed in the nonequilibrium ($\beta > 2.5 \text{ deg min}^{-1}$) or quasiequilibrium mode: All the characteristic effects are present in the DTA curves.

An increase in the heating rate primarily affects the extent to which the reactions occur in the starting solid phase and in the melt. At slow heating (1.25–

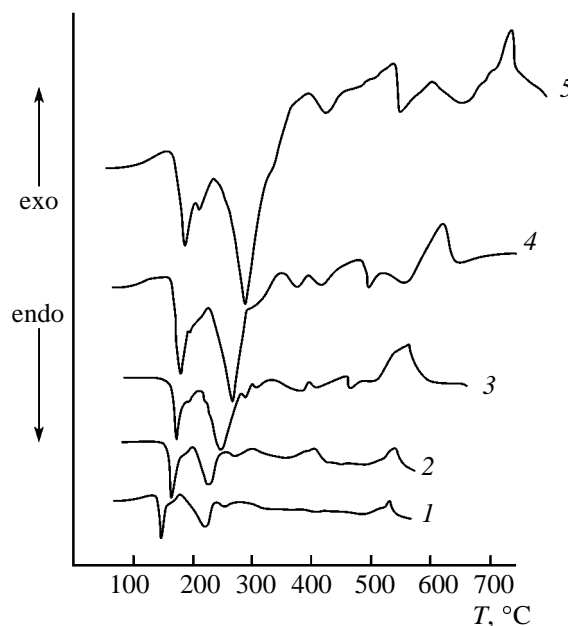


Fig. 1. Heating curves (DTA) of thiourea (m 190 mg). Heating rate, deg min^{-1} : (1) 1.25, (2) 2.5, (3) 5, (4) 10, and (5) 20.

2.5 deg min⁻¹), the composition of the melt above 180°C presumably corresponds to guanidinium thiocyanate, since the band of the NH₄⁺ ion at 1400 cm⁻¹ disappears, whereas the intensity of the band of the SCN⁻ stretching vibrations (2060 cm⁻¹) remains virtually unchanged. At heating rates of 5 deg min⁻¹ and higher, the solid phase is formed from the melt of a mixed composition, CH₅N₃·HSCN–NH₄SCN–SC(NH₂)₂, which is also confirmed by the IR spectra. The range of decomposition of this melt is appreciably shifted toward higher temperatures (Table 1).

The TG curves of thiourea and ammonium thiocyanate (Fig. 2), taken under similar conditions, show apparent similarity above the melting point, confirming that the composition and course of thermolysis of their melts (above 180°C) are identical, which is due to occurrence of reaction (1). Hence, the degree of the Thio isomerization has no appreciable effect on the subsequent decomposition steps, and therefore the reaction kinetics can be studied with pure Thio; preparation of the equilibrium product is unnecessary, which simplifies the experiment.

The layer thickness affects the temperature ranges of melting and decomposition of Thio insignificantly (Table 1). However, as the thickness of the melt layer is decreased, the rate of the weight loss and the maximal degree of the melt decomposition (Fig. 2) somewhat increase, which is due to more efficient heat and mass exchange.

In dynamic experiments, we revealed a weak dependence of the initial rate of the weight loss v_0 on the gas flow rate Q . At 200°C, as Q is increased from 0 to 25 l h⁻¹, v_0 smoothly increases from 0.11 to 0.22–0.23 h⁻¹. Further increase in the gas flow rate had no effect on v_0 , since at $Q \geq 25$ l h⁻¹ the process became kinetically controlled.

Under the conditions of isothermal keeping at temperatures above 185°C, the melt started to boil, and the process continued until the weight loss reached 30–40%. In the course of boiling, hydrogen sulfide was detected in the gas phase near the melt surface, and NH₄SCN condensed on the cold parts of the installation. These facts suggest that the boiling is due to evolution of a large volume of a gas as a result of vigorous reaction (2).

Above 200°C, flashes of red flame were observed over the melt surface. Among the products of thermal decomposition of Thio, only carbon disulfide is highly inflammable (ignition point 120–156°C [6]). Carbon disulfide may form by the reaction [3]

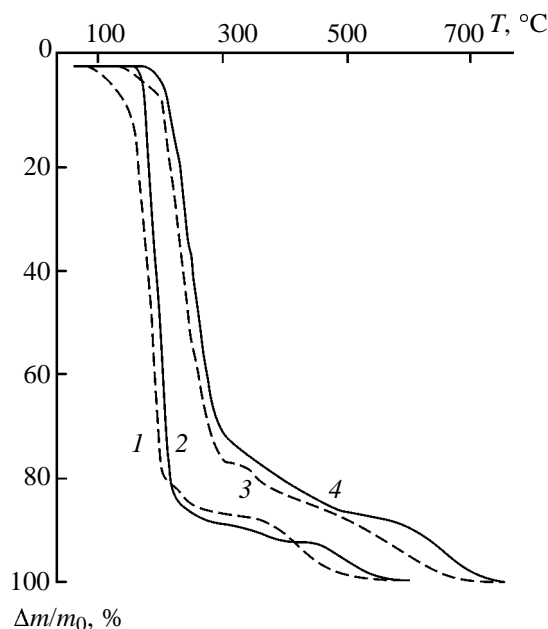


Fig. 2. Heating curves (TG) of (1, 3) ammonium thiocyanate and (2, 4) thiourea, recorded (1, 2) with a thin layer (m 60 mg) at β 1.25 deg min⁻¹ and (3, 4) with a thick layer (m 190 mg) at β 5 deg min⁻¹.

Nitrogen used as flowing gas efficiently suppressed the ignition of CS₂ and the associated uncontrollable self-heating of the melt.

The dynamics of variation of the melt composition was studied by IR spectroscopy of cooled melt samples obtained by isothermal heating at 190°C (Fig. 3). In the IR spectra, the band at 1400 cm⁻¹ belongs to the bending vibrations of the ammonium ion; the

Table 1. Influence of the heating rate on thermal decomposition of thiourea

| β , deg min ⁻¹ | Temperature, °C | | | |
|------------------------------------|-----------------|----------------------------|---|--------------------------------|
| | melting | onset of weight loss | end of third step of thermolysis ^a | complete decom- position |
| 1.25 | 158–160 | 150 | 223 (77.66) | 548 |
| 2.5 | 158–165 | 155 | 230 (77.20) | 550 |
| 5 | 158–175 | 180 | 312 (75.66) | 610 |
| 10 | 158–185 | 190 | 328 (77.40) | 735 |
| 20 | 160–190 | 192 | 360 (74.70) | 854 |
| 1.25 ^b | 158–160 | 158 | 200 (79.10) | 538 |

^a The weight loss (wt %) is given in parentheses. ^b Thin layer (m 60 mg); in other cases, thick layer (m 190 mg).

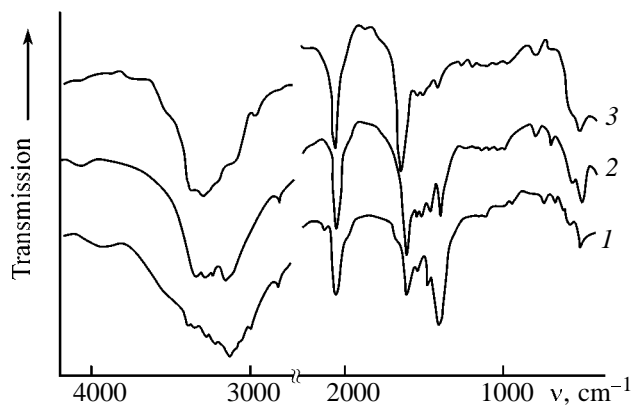


Fig. 3. IR spectra of products of isothermal heating of an $\text{SC}(\text{NH}_2)_2$ melt at 190°C for (1) 1, (2) 3, and (3) 8 h.

bands at 1470 and 1090 cm^{-1} are characteristic bands of Thio; and the bands at 1635 and 500 cm^{-1} are due to vibrations of the guanidinium ion [7].

The melt heated for 1 h was a mixture of ammonium thiocyanate, guanidinium thiocyanate, and a minor amount of Thio. A number of strong absorption bands in the range $3000\text{--}3400\text{ cm}^{-1}$ can be assigned to the stretching vibrations of the amino groups of all the three compounds.

In the IR spectrum of the cooled melt that had been heated for 3 h (after the melt boiling fully ceased), the intensity of the absorption bands of Thio (1470 cm^{-1}) and NH_4^+ (3130 , 1400 cm^{-1}) considerably decreased, whereas that of the guanidinium thiocyanate band noticeably increased.

After heating for 8 h, the melt ceased to lose weight, and its major component was guanidinium thiocyanate. This is confirmed by the absence of the polymorphous transition of NH_4SCN (95°C) in the heating curves of the cooled melt and by the fact that the IR absorption bands of Thio and ammonium thiocyanate at 1470 , 1400 , and 1090 cm^{-1} were on the background level (Fig. 3). At the same time, as judged from the intensity of the bands at 2060 , 1635 , and 500 cm^{-1} , the amount of guanidinium thiocyanate remained virtually unchanged compared to the previous sample.

Hence, reaction (2) does not fully stop after the end of boiling, since isomerization (1) starts to proceed in the reverse direction, slowly compensating the loss of Thio from the melt.

Thus, under isothermal conditions at 190°C , reactions (2) and (3) occur successively, and the reactive cyanamide formed by reaction (2), apparently, instantaneously transforms by reaction (3) into guanidinium

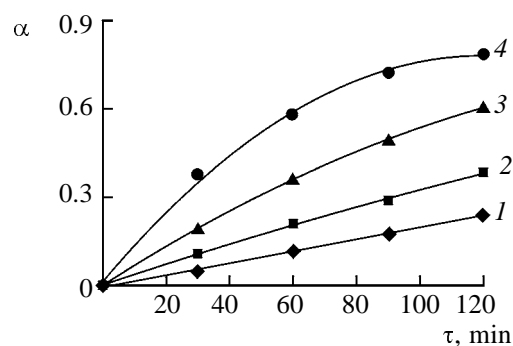


Fig. 4. Kinetic curves of thermal decomposition of thiourea in a nitrogen flow: (1) 181 , (2) 190 , (3) 200 , and (4) 210°C .

thiocyanate. Ammonium thiocyanate, isomerizing into Thio, supports this process. Cessation of the weight loss corresponds to complete decomposition of both Thio and NH_4SCN and formation of a homogeneous melt of guanidinium thiocyanate, stable at the given temperature.

Figure 4 shows the kinetic curves of thermal decomposition of the melt in the coordinates degree of conversion α –time of isothermal heating. The calculated kinetic parameters of thermal decomposition of thiourea under isothermal and nonisothermal conditions are listed in Table 2. Additionally we calculated the activation energy from the linear dependence of $\log(1/\tau_{0.5})$ on $1/T$ ($\tau_{0.5}$ is the conversion half-time); we obtained the value of 117.2 kJ mol^{-1} .

The results of the nonisothermal experiments are affected by the endoeffect of the Thio melting. Therefore, E was determined with a larger error than from the isothermal experiments. However, the correlation between the values of E obtained by different methods (under isothermal conditions, gravimetrically; under nonisothermal conditions, from DTA curves) shows that this parameter, on the whole, has been determined with a reasonable accuracy and that it characterizes formation of guanidinium thiocyanate.

Since reaction (2) is the limiting step, formation of activated complexes presumably involves hydrogen bonding between the sulfur atom of one Thio molecule and amino group protons of another molecule. Then the most significant contribution to the activation energy will be made by cleavage of the C–S bond whose energy in the Thio molecule is 100.5 kJ mol^{-1} [8].

On reaching 60–70% degree of decomposition under isothermal conditions, opalescence appeared

Table 2. Kinetic parameters of formation of guanidinium thiocyanate

| Isothermal conditions | | | | | Nonisothermal conditions | | |
|-----------------------|----------|---|--|--|------------------------------------|-------------------|--|
| <i>T</i> , K | <i>n</i> | $(k \pm \Delta k) \times 10^3$, min ⁻¹ | $E \pm \Delta E$, kJ mol ⁻¹ | $A \times 10^{-10}$, min ⁻¹ | β , deg min ⁻¹ | T_{\max} , K | $E \pm \Delta E$, kJ mol ⁻¹ |
| 454 | – | 2.20 ± 0.26 | 114.5 ± 6.4 | 2.3–4.9 | 1.25 | 441 | 100.9 ± 28.5 |
| 463 | 0.84 | 3.93 ± 0.20 | | | 2.5 | 455 | |
| 473 | 0.91 | 7.64 ± 0.23 | | | 5 | 465 | |
| 483 | 1.28 | 13.61 ± 1.17 | | | 20 | 487 | |

in a melt, followed at temperatures above 200°C by coagulation of amorphous solid particles. In the process, the rate of the weight loss appreciably decreased. This corresponded to transition from the second step of thermolysis of the melt to the third step.

In the course of the third step, solid products of the *s*-triazine (melamine, melam) and *s*-heptazine (melem) structures [9] precipitate from the melt.

The activation energy of the third step (Table 3) characterizes pyrolysis of guanidinium thiocyanate, involving deamination and multistep condensation of the $-\text{NH}(\text{NH}_2)\text{C}-$ groups: first into *s*-triazine rings and then into *s*-heptazine cores. The latter species fully dissociate into gaseous compounds with increasing temperature, after a series of transformations (Table 1, Fig. 2).

EXPERIMENTAL

The IR absorption spectra were recorded on a Record IR-75 spectrophotometer using KBr techniques. The content of substances in pellets (*d* 15 mm) was 0.5 wt % for pure substances and 1 wt % for cooled melts. The pellet weight was constant to within $\pm 2 \times 10^{-4}$ g.

Coarsely crystalline thiourea and chemically pure grade ammonium thiocyanate were dried at 60°C for 3–4 h before use.

The curves of nonisothermal heating (to 1000°C) were recorded in air with a Q-1500D derivatograph. The sample holders were from the standard kit: a conical platinum crucible (diameter at half-height *d* 9 mm, height *h* 12 mm) and a cylindrical quartz crucible (*d* 6, *h* 15 mm, wall thickness ≤ 0.5 mm).

The method of continuous weighing in the isothermal mode, applied in [10] to studying sublimation of Thio on heating to 180°C, proved to be unsuitable because of vigorous evolution of thermolysis products and their subsequent condensation on cold parts of the installation. Therefore, we used the classical method of gravimetric analysis.

Conical porcelain crucibles (*d* 18, *h* 30 mm) were charged with samples weighed on an analytical balance with an accuracy of $\pm 2 \times 10^{-4}$ g. The crucibles were placed in a preheated aluminum thermostat arranged in a muffle oven. The temperature was measured with a Chromel–Alumel thermocouple in the central crucible. The time was counted since the moment when the melt temperature reached the prescribed level. In the course of the experiment, the melt temperature was maintained with a $\pm 1.5^\circ\text{C}$ accuracy. After definite periods, the crucibles were successively removed from the oven, cooled, and weighed on an analytical balance. Experiments were performed at various nitrogen flow rates. For this purpose, an inlet tube connected to a gas system was arranged in the rear wall of the oven. The outlet tube was arranged in the oven door and could be connected to a foam flow meter.

From the results of isothermal measurements, we calculated the degree of conversion $\alpha = (m_0 - m)/\Delta m_{\max}$, where m_0 is the initial melt weight (1.5 g); m , current melt weight; and Δm_{\max} , maximal weight loss of the melt. In the temperature range 180–220°C, Δm_{\max} is 1.075 ± 0.010 g.

Under isothermal conditions, the reaction order was calculated from each kinetic curve, and the rate constants, from the first-order kinetic equation [11].

Table 3. Kinetic parameters of pyrolysis of the melt based on guanidinium thiocyanate (nonisothermal conditions)

| β , deg min ⁻¹ | T_{\max} , K | <i>n</i> | $E \pm \Delta E$, kJ mol ⁻¹ |
|------------------------------------|----------------|----------|--|
| 1.25 | 431 | 1.095 | 76.3 ± 11.4 |
| 2.5 | 503 | 1.120 | |
| 5 | 523 | 0.980 | |
| 10 | 541 | 1.032 | |
| 20 | 571 | 1.214 | |

Figure 2 shows that, under the linear heating conditions, the second and third steps are not clearly resolved in the TG curve; therefore, to calculate the kinetic parameters under nonisothermal conditions, we used the DTA curves (Fig. 1) in which the temperatures of the extrema are determined fairly accurately even at partial overlap of the effects. The reaction orders and activation energies were calculated by the Kissinger method [12].

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