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INVESTIGATION OF THERMAL DECOMPOSITION OF ETHYLENEBISDITHIOCARBAMATE ACID, ITS DIAMMONIA SALT AND β-AMINO-ETHYL-DITHIOCARBAMATE

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ABSTRACT

Thermal decomposition of three dithiocarbamate species has been studied by TG, DTG and DTA methods. The mechanism of it has been proposed and activation energies as well as reaction orders have been calculated.

INTRODUCTION

Some salt of ethylenebisdithiocarbamate acid are known as effective fungicides, e.g. zinc or manganese salts. The thermal properties of these compounds were investigated by several authors [1,2], however, those of ethylenebisdithiocarbamate acid /H_2EBDTC/, its diammonia salt / /$NH_4/_2$EBDTC / and β-amino-ethyl-dithiocarbamate up to now have been unknown.

EXPERIMENTAL

C h e m i c a l s. Acid H_2EBDTC was prepared by adding of H_2SO_4 to Na_2EBDTC.$6H_2O$ water solution. The precipitated white crystals were filtrated and dried at ambient temperature in an exsiccator with P_4O_{10}. The found /calculated/ composition is: % C - 22.50 /22.62/, % N - 13.17 /13.19/, % H - 3.86 /3.79/.

/$NH_4/_2$EBDTC was prepared in solid state by the decantation of /$NH_4/_2$EBDTC water solution by aceton until the white crystalline matter falls out. The found /calculated/ composition is : % C - 19.72 /19.49/, % N - 21.90 /22.74/, % H - 5.58 /5.73/.

β-amino-ethyl-dithiocarbamate was prepared by the vacuum evaporation of /$NH_4/_2$EBDTC water solution at 60-70°C and recrystallization of the obtained light yellow crystalline matter.

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The found /calculated/ composition is : % C - 27.04 /26.45/, % N - 20.85 /20.56/, % H - 6.13 /5.92/.

I n s t r u m e n t a t i o n. The thermal decomposition records were obtained by Derivatograph OD-102 /MOM, Budapest/ with photographic registration. The weighted amount was 100 mg in all measurements, Al_2O_3 was used as a standard. The temperature scan was 6°C per min, the temperature range was 20-600°C. All measurements were performed in nitrogen atmosphere.

RESULTS AND DISCUSSION

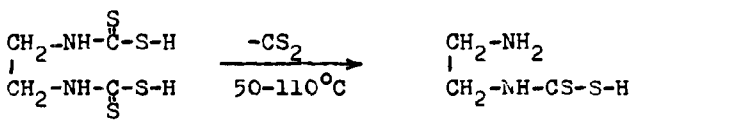
From the course of TG, DTG and DTA curves at the thermal decomposition of acid H_2EBDTC it can be seen that the decomposition proceeds in four endothermic processes with the following relative mass decrease values : 32.0, 20.0, 30.5 and 17.5 %.

If we consider the first process /50-110°C/ as a releasing of one molecule CS_2 and the second one /80-130°C/ as a releasing of one molecule H_2S, the theoretical relative mass decrease value are 35.85 and 16.04 % respectively.

The small difference between the experimental and theoretical values is caused by the difficulty in the individual reactions separation. The final product of the two above mentioned steps is ethylenethiourea /ETU/ which decomposes in the third process /180-240°C/ into HSCN /theoretical decrease value is 27.80 %/ and aziridine C_2H_5N. The last reaction is the decomposition of aziridine under formation of NH_3 and C_2H_2 at 400-540°C /theoretical decrease value is 20.31 %/.

The thermal decomposition of acid H_2EBDTC can be written on the whole as follows :

Step 1



β -amino-ethyl-dithiocarbamate

Step 2 $CH_2(-NH_2)-CH_2-NH-CS-S-H \xrightarrow[80-130^{\circ}C]{-H_2S} CH_2(-NH-)-CH_2-NH\diagup C=S$ ETU

Step 3 $CH_2(-NH-)-CH_2-NH\diagup C=S \xrightarrow[180-240^{\circ}C]{-HSCN} CH_2-CH_2\diagup NH$ aziridine

Step 4 $CH_2-CH_2\diagup NH \xrightarrow[400-540^{\circ}C]{} NH_3 + C_2H_2$

The activation energy values and the reaction orders were calculated according to Freeman et al. [3] from the equation /1/ by least-squares methods.

$$\frac{-E^{*}/R \cdot \Delta/T^{-1}/}{\Delta \ln w_r} + a = \frac{\Delta \ln dw/dt}{\Delta \ln w_r} \qquad /1/$$

where E^{*} - activation energy, R - universal gas constant, $w_r = w_c - w$ /w_c - total relative mass decrease, w - actual relative mass decrease/, a - reaction order, T - temperature.

The E^{*} and a values and their standard deviations were calculated with the aid of program C17DTG and are presented in Table 1.

The thermal decomposition of $/NH_4/_2$EBDTC consists of three endothermic separate processes with the relative mass decrease values 55.5, 26.0 and 18.5 %.

Common splitting off H_2S, CS_2 and $2NH_3$ under ETU formation is the first reaction step /70-150°C/ since good agreement between the theoretical /58.54 %/ and the experimental /55.5 %/ value of mass decrease was found and because of analogy with the thermal decomposition of acid H_2EBDTC.

The second /150-300°C/ and the third /320-550°C/ reaction is identical with the third and fourth one observed at thermal decomposition of acid H_2EBDTC. The calculated mass decreaee value for the second reaction is 23.99 %, for the third one 17.47 %. The calculated E^{*} and a values are presented in Table 2.

The thermal decomposition of β-amino-ethyl-dithiocarbamate proceeds in three steps which confirm the suggested thermal decomposition of acid H_2EBDTC and /NH_4/$_2$EBDTC as well.

The first step /130-140°C/is undoubtedly the releasing of H_2S under ETU formation /found 24.0 %, calculated 25.02 %/. The second step /230-300°C/ is the releasing of HSCN from the molecule ETU /found 47.0, calculated 43.37 %/. The third step /340-600°C/ is the decomposition of aziridine into NH_3 and C_2H_2 /found 29.0 %, calculated 31.61 %/.

The temperature ranges in which the above described reactions proceed confirm also the proposed mechanism in the H_2EBDTC and /NH_4/$_2$EBDTC decomposition. The calculated E^* and a values are presented in Table 3.

Table 1. Thermal decomposition of H_2EBDTC.

Reaction	E^*/ kJ/mol	ΔE^*/ kJ/mol	a	Δa
1	112.5	1.94	-0.499	0.223
2	58.9	4.13	0.518	0.064
3	154.4	11.1	1.070	0.216
4	147.1	7.14	1.055	0.159

Table 2. Thermal decomposition of /NH_4/$_2$EBDTC.

Reaction	E^*/ kJ/mol	ΔE^*/ kJ/mol	a	Δa
1	53.2	1.93	-1.460	0.320
2	132.5	3.23	0.959	0.100
3	80.7	3.23	1.110	0.140

Table 3. Thermal decomposition of β-amino-ethyl-dithiocarbamate.

Reaction	E^*/ kJ/mol	ΔE^*/ kJ/mol	a	Δa
1	247.5	3.01	1.589	0.038
2	198.3	24.0	1.239	0.392
3	129.7	9.10	1.690	0.189

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