

INVESTIGATION OF UROTROPINE THERMAL DECOMPOSITION REACTION IN
SELF-GENERATED ATMOSPHERE BY MEANS OF THERMAL ANALYSIS METHOD

Evgeni A.Gusev,^X Sergei V.Dalidovich, Lidiya I.Krasovskaya,
Byelorussian State University
Minsk, USSR

ABSTRACT

Urotropine decomposition in self-generated atmosphere was studied by means of differential thermal analysis. It was found out that under such conditions the urotropine was not sublimated with heat absorption as in case of investigations in the air or in the vacuum. At constant volume the urotropine decomposition enthalpy amounted to -98 ± 5 kJ/mol. By means of mass-spectrometric, gas-chromatographic and X-ray analysis we identified pyrolysis products, which were hydrogen, nitrogen, ammonia, methane, methylamines and amorphous tar-form sediment.

INTRODUCTION

Several papers were concerned with urotropine thermal decomposition reactions (ref.1-4). The results of investigations relating to kinetics, pyrolysis products were cited and decomposition reaction mechanism was discussed in these papers. However, in scientific literature we could not find any data concerning the urotropine decomposition enthalpy that was connected with its sublimation at heating in the air or in the vacuum. Investigation technique of substance pyrolysis in self-generated atmosphere, used in this paper made possible to obtain the reliable meaning of the urotropine decomposition enthalpy and to determine more precisely its gaseous products.

MEASURING METHODS

The urotropine possessed a reactive purity and was additional cleaned by a vacuum sublimation. Thermal analysis was carried out in a dynamic calorimeter of triple heat bridge (ref.5) in the range of 150-700 K. The sample was disposed in an ampoule made of stainless steel which had a volume of 0,9 ml. Density of charge was 35-40 mg/ml. Such ampoules resisted pressure up to 15 MPa. Before being sealed the ampoules with the sample was blown off by Ar. Heating rate was 2 K/min. After decomposition the ampoules were cooled in the calorimeter up to 100 K, and then they were

heated again. Some urotropine pyrolysis products was determined according to peaks on the thermal curve obtained. Then ampoules were opened and gaseous products were analyzed in a MAT-311 mass-spectrometer and in a LCM-69 chromatograph. Solid products were studied in a DRON-1,5 X-ray diffractometer.

RESULTS AND DISCUSSION

In Fig.1 there are the results of the urotropine decomposition reaction thermal analysis in the air (DTA, curve "a") and under pressure of self-generated atmosphere ("b" and "c" curves). It is known that the urotropine is sublimated with decomposition at atmospheric pressure and at 536 K. According to DTA curve it follows that the urotropine sublimation takes place in the range of 530-550 K for all that if there is a decomposition, than it occurs in a gaseous phase and its quantity is rather small. Sublimation enthalpy cited in the paper (ref.6) is equalled to $+74,9 \pm 2,9$ kJ/mol. As it is seen from the Fig.1 the urotropine decomposition in an ampoule occurs with a heat liberation in the same temperature range that of sublimation. The urotropine decomposition enthalpy at the constant volume was -98 ± 5 kJ/mol. The comparison of the value obtained at the formation enthalpy of $+124,1 \pm 0,8$ kJ/mol (ref.6) shows strong evidence for the urotropine to be decomposed with a formation of not only simple but and complex both solid and gaseous substances. Detailed analysis of the urotropine pyrolysis products is given in the paper (ref.2). Black solid sediment and oily substances were found along with gaseous substances. The main gaseous products were ammonia, methan and in a less number there were hydrogen and nitrogen (ref.2).

Repeated heating of the ampoule with the urotropine pyrolysis products (Fig.1, curve "c") made possible to reveal a number of substances (1,2,3 peaks). These substances could be finally identified only by means of mass-spectrometric and gas-chromatographic analysis. In order to carry out these analysis the ampoule was opened in a special device. H_2 and CH_4 were found by gas-chromatographic analysis. The rest of the products (NH_3 , mono-, di- and trimethylamin, H_2 , C_2H_4 , HCN) were identified by a mass-spectrometric method. The last four substances being in the form of an admixture, for instance HCN content was in 20 times less than that of NH_3 . In accordance with these results the peaks on "c" thermal

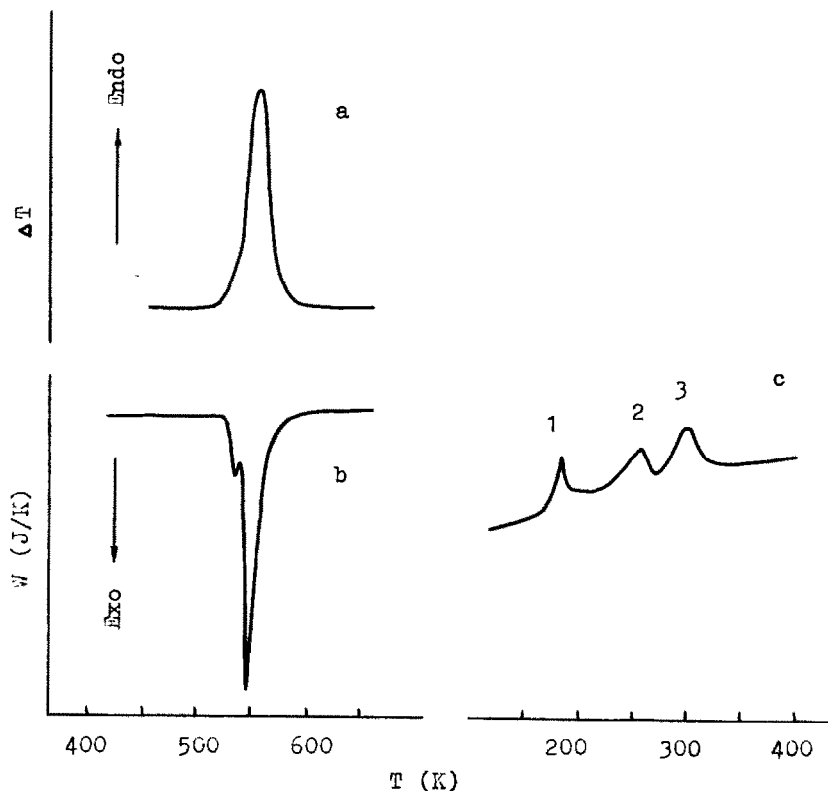


Fig.1 Thermal curves of urotropine in the air (DTA, curve "a") and in sealed ampoule ("b"-initial sample, "c"-pyrolysis products).

curve can be related to ammonia (2-nd peak - evaporation), ammonia mixing with methylamines (1-st peak - melting) and to methylamines mixture (3-rd peak - evaporation). In this case no oily substances were found. All the inside surface of the ampoule was coated by a black glittering solid deposit which content was equal to 72 weit % of initial sample mass. Carbon content in the black deposit was 60,4%. X-ray method showed that this product was amorphous. Apparently, at the urotropine pyrolysis a polymer product was formed with the greater content of both combined and free carbon.

In accordance with data obtained we can assume a mechanism of the urotropine decomposition in self-generated atmosphere. At

heating the breakage of bonds nitrogen-carbon takes place and most probably methylamines are the initial products of decomposition. For ammonia formation it is necessary that hydrogen atoms pass from carbon to nitrogen (ref.2).

At the same time the presence of methane and methylamines in pyrolysis products would enable to draw a conclusion that there is a possibility of hydrogen atom transitions from carbon not only to nitrogen but also to the next carbon atom. All the possible reactions going in both concentrated and gaseous phase are proceeding in a narrow temperature range that is confirmed by the one peak on the thermal curve. The presence of the peak on the curve "b" at a temperature of 532 K can be explained by its partly sublimation which takes place at the beginning of the urotropine decomposition.

REFERENCES

- 1 G.Klipping, I.N.Stranski, Z. anorg. allg. Chem. 297 (1958) 23
- 2 A.F.Bogenschutz, G.Klipping, I.N.Stranski, Z. anorg. allg. Chem. 299 (1959) 69
- 3 I.N.Stranski, G.Klipping, H.-G.Maenning, Z. elektrochem. 63 (1959) 135
- 4 D.Hoene, G.Klipping, I.N.Stranski, Chem. Ber. 93 (1960) 2782
- 5 A.A.Vecher, A.G.Gusakov, A.A.Kozyro, Russ. J. Phys. Chem. 53 (1979) 783
- 6 M.Mansson, N.Rapport, E.F.Westrum, J. Amer. Chem. Soc. 92 (1970) 7296