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Note

THERMAL ANALYSIS OF α,β-DIAMINOPROPIONIC ACID MONOHYDROCHLORIDE

JERZY BŁAŻEJOWSKI

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

ANDRZEJ CZERWIŃSKI and RYSZARD ANDRUSZKIEWICZ

Department of Pharmaceutical Technology and Biochemistry, Technical University, 80-952 Gdańsk (Poland)

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The biological activity of many organic compounds may be modified by even minor changes in their structure. Such changes can be introduced using adequate substrates for synthesis. The required modifications of the structure of biologically active molecules can also be achieved upon influence of some external factors such as temperature, pressure, electromagnetic radiation, ionizing radiation and so on. Temperature appears to be the most frequently used factor for this purpose. The behaviour of chemical substances upon heating is easy to examine by thermal analysis methods. Thus, these methods were also applied in the present work to investigate the thermal properties of α,β-diaminopropionic acid monohydrochloride.

Generally, the biologically active molecules have complex structures. Therefore, one might expect a complex course of thermal reactions for such compounds. In order to gain a clearer picture of the thermal processes which may take place it is necessary to examine the thermal behaviour of simpler constituents of biologically active molecules. One such compound is α,β-diaminopropionic acid. This non-protein amino acid has been shown to be the constituent of a number of biologically active compounds, mainly antibiotics; it has been found in hydrolysates of peptide antibiotics, e.g. bleomycin [1], capreomycins [2], tuberactinomycins [3], tallysomycins [4] and edeines [5].

EXPERIMENTAL

α,β-Diaminopropionic acid monohydrochloride was prepared by the method of Kitagawa et al. [6].

Thermal analyses were performed on a Monicon OD-103 derivatograph

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with α-Al_2O_3 as a reference, in a dynamic atmosphere of nitrogen. Other operating conditions are listed at Fig. 1.

The isothermal thermolyses were carried out in a device previously described (ref. 7, Fig. 1b).

RESULTS AND DISCUSSION

The compound studied presents a multi-step thermal decomposition pattern (Fig. 1). The mass loss corresponding to the first step indicates the release of one molecule of NH_4Cl from one molecule of the substrate. To support this suggestion thermolysis was carried out in the isothermal conditions at temperature corresponding to the beginning of the decomposition (495 K). Indeed, under these conditions the formation of a white precipitate on the cooled part of the apparatus was observed. The deposit was identified

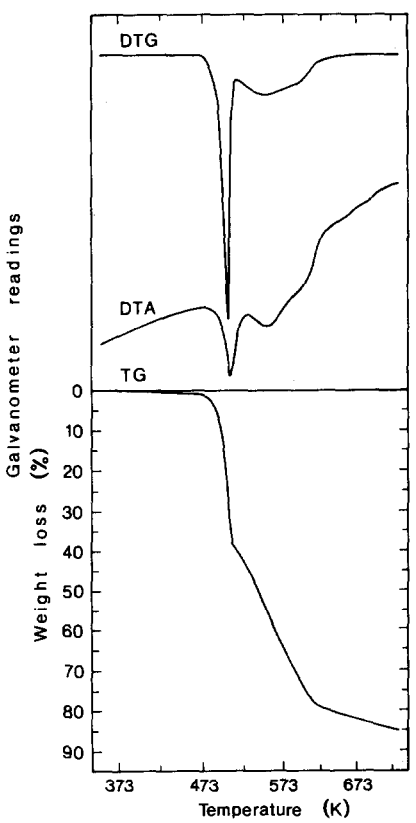
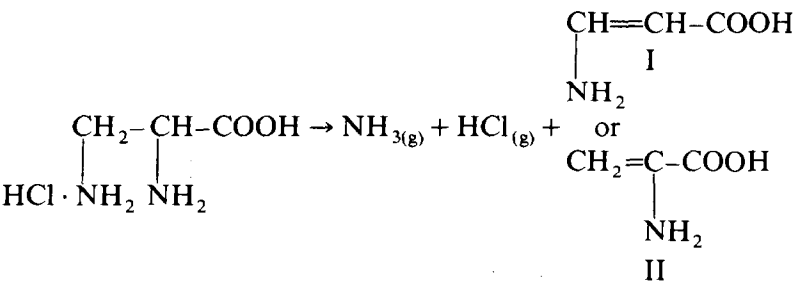


Fig. 1. Thermal analysis of α,β-diaminopropionic acid monohydrochloride. Mass of sample, 100 mg; heating rate (Φ), 5 K min^{-1}; sample holder, platinum crucible. Galvanometer sensitivities: DTG = 1/10, DTA = 1/3 and TG = 100 mg.

as NH_4Cl. The foregoing facts indicate that thermolysis of the compound in the first step proceeds according to the scheme



Since the peak temperatures, in DTA and DTG, of the first step are slightly higher than those for the sublimation process of NH_4Cl [8], one may expect that during the decomposition process both constituents of NH_4Cl, namely NH_3 and HCl, appear in the gaseous phase.

The structures of compounds I and II were proposed assuming α or β elimination mechanisms for the release of the NH_4Cl molecule. Investigations leading to the identification of these compounds proved unsuccessful, presumably because of their low thermal stability. Based on the general knowledge of the thermal reactions of amino acids [9], the β-elimination mechanism seems to be more probable.

Careful analysis of the TG and DTG curves indicated that the first decomposition stage is not overlapped by the following thermolysis steps up to the α value (corresponding to the release of NH_4Cl) equal to 0.8. Thus, the application of the computational procedures previously described [8,10] seems justified for the estimation of the thermodynamic and kinetic parameters of the process.

The enthalpy change for the first step of thermolysis was evaluated using an approximate method of Stepin et al. [11]. On the basis of the five replicate experimental runs a value of ΔH_r^0 equal to 4.99 (± 0.07) $\times 10^5$ J mol^{-1} was evaluated. The above value of ΔH_r^0 is more than three times higher than that describing the sublimation process of NH_4Cl [8] (1.57×10^5 J mol^{-1}), which means that the formation of the products I and II requires a large amount of energy. Thus, any of these products should be thermodynamically unstable.

The kinetics of the first step of thermolysis of α,β-diaminopropionic acid monohydrochloride were examined using a standard treatment described elsewhere [10]. In the search for an adequate form of kinetic equation, criteria described previously [8,10] were applied. Some values of the kinetic constants corresponding to the equations describing most satisfactorily the first step of thermolysis are listed in Table 1.

Reviewing the full set of values calculated it was observed that the functions $g(\alpha)$ or $f(\alpha)$ [12] corresponding to the mechanisms P1, P2, P3 and P4 give the best fit to the experimental data. These mechanisms are,

TABLE 1

Kinetic constants for the thermolysis of α,β-diaminopropionic acid monohydrochloride [a]

Method of evaluation of kinetic constants [c]	Symbol of the mechanism [b]				
	R1	R2	P1	P2	D1
	E *Z*	*E* *Z*	*E* *Z*	*E* *Z*	*E* *Z*
A: eqn. (8)	2.15 05	2.44 05	1.59 05	1.41 05	4.39 05
in ref. 10	1.4 21	1.5 24	9.0 14	7.6 12	5.6 45
B: eqn. (9)	2.19 05	2.48 05	1.64 05	1.45 05	4.43 05
in ref. 10	7.0 19	6.7 22	6.0 13	5.8 11	1.3 44
C: eqn. (10)	2.14 05	2.42 05	1.59 05	1.40 05	4.35 05
in ref. 10	1.0 21	1.1 24	8.6 14	6.4 12	2.6 45
E: eqn. (12)	2.18 05	2.47 05	1.63 05	1.45 05	4.39 05
in ref. 10	5.5 19	4.4 22	5.4 13	5.2 11	6.1 43
F: eqn. (13)	2.89 05	3.56 05	2.34 05	2.15 05	5.11 05
in ref. 10	8.2 28	5.2 36	5.3 22	4.2 20	2.2 53
G: eqn. (14)	2.94 05	3.60 05	2.38 05	2.19 05	5.14 05
in ref. 10	2.9 27	3.7 34	2.2 21	2.0 19	4.4 51

[a] Calculations were performed on a TI 59 calculator. Values are presented in computer notation, e.g., $5.00\ 05 = 5.00 \times 10^5$. E = Apparent activation energy (J mol^{-1}); Z = constant (s^{-1}). Values of E and Z listed were taken as the means from five replicate measurements.

[b] Table 1 in ref. 12.

[c] Methods of evaluation of kinetic parameters utilize the equations

A and C: $g(\alpha) = T^2 \frac{ZR}{\Phi E} \exp(-E/RT)$

B and E: $g(\alpha) = T \frac{Z}{\Phi} \exp(-E/RT)$

F: $d\alpha/dT = f(\alpha) \frac{Z}{\Phi} \exp(-E/RT)$

G: $d\alpha/dT = f(\alpha) \frac{Z}{\Phi} (1 + E/RT) \exp(-E/RT)$

however, less probable since they predict much lower values of the activation energy compared with the value of the enthalpy change for the process. Further, the R1 mechanism may be considered as the rate-controlling process followed by R2 and D1 mechanisms. It may also be noticed that differential methods led to the higher values of the kinetic constants compared to those resulting from application of integral methods.

All reaction mechanisms chosen, based on the values of the statistical functions $|r|$ and δ, predict values of E lower than the value of ΔH_r^0. This discrepancy seems to be ascribable to the contributions to ΔH_r^0 from the fast reaction stages other than the rate-controlling process.

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