Thermochimica Acta, 93 (1985) 45-48
Elsevier Science Publishers B.V., Amsterdam

THE STUDY OF THERMAL CYCLIZATION OF 4-AMINOSUBSTITUTED-1,3-DIMETHYL-5-NITROSOURACILS

Peter Králik, P.J.Šafárik University
Košice, Czechoslovakia
Ladislav Štibrányi, Slovak Technical University
Bratislava, Czechoslovakia
Tatiana Gondová, P.J.Šafárik University
Košice, Czechoslovakia
Michal Hirjak, Slovak Technical University
Bratislava, Czechoslovakia

ABSTRACT

The thermal behaviour of some nitrosouracils have been studied by means of DSC calorimetry. The observed exothermic cyclocondensation of the titled compounds have been evaluated together with the purity of the praducts obtained. The role of the structure changes is discussed.

INTRODUCTION

The synthesis of organic compounds is prevailingly performed in solution. Little attention has been paid to this type of reactions in solid state. On the other hand the study of the thermostability of organic compounds such as explosives, pharmaceuticals etc. has been often studied by thermoanalytical methods. The first paper dealing with the DTA application in the observation of the synthesis of organic substances is probably that one published by Chiu (1). In the meantime DSC has been also used for this purpose (2), for the study of charge transfer complexes (3) and molecular rearangement (4) as well as for the estimation of the heat of reaction (5) and the heat of formation (6).

Some uracils were found to undergo the cyclocondensation upon thermal treatment (7,8). The aim of this work is to present a complex evalution of the thermoanalytical study of cyclocondensation process in the solid state using some nitrosouracils as example.

Proceedings of ICTA 85, Bratislava

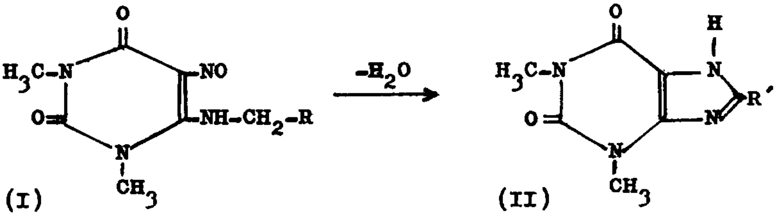
MEASURING METHODS

The substances were weighed in the range 0.8 - 1.0 mg range on Mettler ME-22 microbalance in volatile aluminium sample pans. The calerimeter DSC-2 (Perkin Elmer) was calibrated using indium and saphire in similar pans. The thermograms were obtained using sensitivity range of 0.5 $mcal.s^{-1}$ and heating rate 5 $K.min^{-1}$. The pans were provided with pineholes.

The compounds were prepared by the reaction of chloride of 1,3 - dimethylbarbituric acid with substituted amines and the product obtained was nitrosated with propylnitrite in CH_3OH. Purified compounds were tested by elemental analysis and spectroscopic methods.

RESULTS AND DISCUSSION

During the heating of substances under investigation two peaks can be observed. The thermogram of 1,3 - dimethyl-5-nitroso-4-methylaminouracil is shown in Fig.1. The cyclocondensation reaction can be described by the following reaction:



(I) (II)

The product can be identified by its melting endotherm occured at higher temperature. The nature of condensation products can be expected to be influenced by the structure of the reacting materials e.g. by the structure changes due to the variation of the substituents (R=H; $CH_2C_6H_5$; CH_2COOCH_3). Besides the heats of reaction the molar heat capacities of reactants and products were estimated in the temperature range 335 - 369 K and 455 - 489 K as well as 335 - 363 K and 445 - 479 K in order to characterize better the structural differences. A linear relationship $C_p = A + BT$ was found out using the least square method for each of the derivate (Tab.1). The method of group additivity described by Benson and Buss (9)

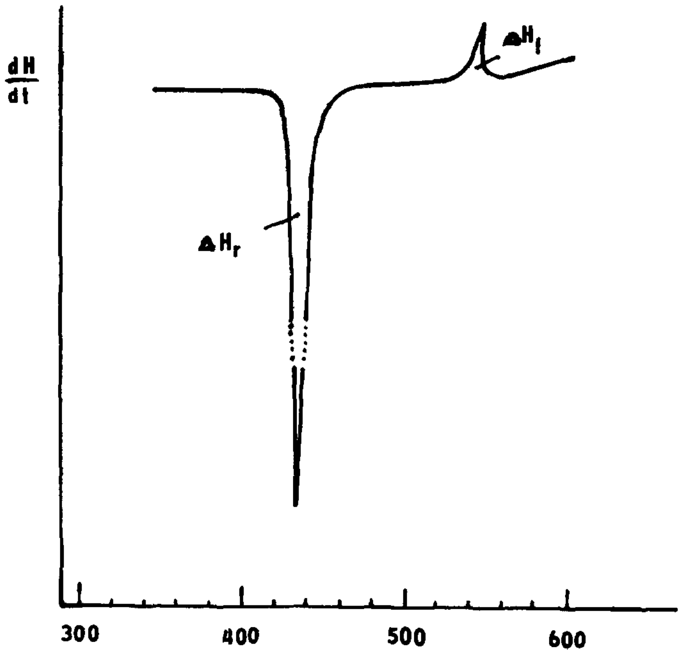


Fig.1 DSC thermogram of 1,3-dimethyl-5nitroso-4-methylaminouracil

Tab.1. The constants of linear relationship of molar heat capacity

sample R=	A $JK^{-1}mol^{-1}$	B $JK^{-2}mol^{-1}$	stand. dev.
R= H	18,8	0,74	1,27
R'= H	-360,8	1,50	2,59
R=$CH_2C_6H_5$	-523,9	2,76	4,64
R'=$CH_2C_6H_5$	224,8	0,58	2,13

was applied in order to compare the calculated and experimental values of heat of reaction given in Tab.2. For the substance with R = $CH_2C_6H_5$ was obtained a relatively good agreement (ΔH_{r-calc} = -201,63 $kJ.mol^{-1}$). It should be mentioned that the exothermic reaction enthaplies were not corrected for the enthalpies of melting of the reactants and enthalpies of crystalization of products. Namely it was found out by thermomicroscopical observation that in the first step the reactants were melted followed by next step characterized by color change due to the formation of the respective purine.

The slight differences in ΔH_r can be ascribed to the substitution if one takes into account the steric effects. The same effect can be observed in the differences in C_p values, which may be due to the relative mobility of methyl and benzil goups.

Tab.2. Reaction enthalpies, peak temperatures and conversion.

sample R=	ΔH_r $kJ.mol^{-1}$	T_p K	release of H_2O (%) teor.	 exper.
H	-191,8	425,5	9.09	10.18
$CH_2C_6H_5$	-248,3	423.0	6.25	6.28
CH_2COOCH_3	-224,8	400,0	-	-

The weight decrease in third case was not estimated because of sublimation of the product. Probably the higher exper. value at the first derivate is also connected with this effect. Finally the purity of benzil derivate was found to be 99.6% with 1% linearization. This corresponds to high degree of conversion.

CONCLUSION

Thus, DSC has shown to be a suitable method to study the cyclocondensation of titled uracils and to characterize the products formed by this process.

REFERENCES

1 J. Chiu, Anal. Chem. 34 (1962) 1841
2 E.W. Crandall, M. Pennington, J. Chem. Educ. 57 (1980) 824
3 L. Abate, G. Syracusa, Thermochim. Acta 29 (1979) 157
4 C.W. Bird, I.J. Patridge, C.K. Wong, Tetrahedron 37 (1981) 1011
5 A.K. Srivastava, Z. Phys. Chem. 4 (1979) 630
6 J.S. Brennan, N.M.D. Brown, F.L. Swinton,
J. Chem. Soc. Faraday Trans. 1 (1965) 70
7 H. Goldner, G. Dietz, E. Carstens, NDR Pat. 50614 (19.2.1965)
8 H. Kamashina, I. Kumastino, Jap. Pat. 7002384 (27.1.1970)
9 S.W. Benson, J.H. Buss, J. Chem. Phys. 29 (1958) 546