KINETIC STUDY OF THE THERMALLY INITIATED CYCLOCONDENSATION OF SOME 1,3-DIMETHYL-4-ALKYLAMINO-5-NITROSOURLACILS

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The isothermal and non-isothermal DSC method was used to investigate the influence of changes in structure of 1,3-dimethyl-4-alkylamino-5-nitrosouracils on the 8-substituted theophyllines originating in the cyclocondensation reaction. The evaluation of the optimum reaction mechanism obtained on the basis of the corresponding model functions by using the integral method of Coats and Redfern is discussed. Significant differences, depending on the nature of the substituents, were observed in the course of the reaction.

The thermoanalytical methods have become indispensable in the study of thermal properties of substances. In most cases these methods are used to investigate the thermal decompositions of inorganic compounds, organic polymers, etc. [1–3]. The results of such studies also contribute to characterization of the processes of destruction taking place in the course of heating.

The study of substances from which qualitatively different products originate on heating is an equally important field of use of these methods, though a relatively small number of papers are concerned with these problems [4–6]. The thermally initiated cyclocondensation of 1,3-dimethyl-4-alkylamino-5-nitrosouracils (I), which is the basis of one of the methods of synthesis of the 8-substituted theophyllines (II) [7], is one such process:

\[
\begin{align*}
I & \xrightarrow{\Delta} II \\
\text{H}_3\text{C} & - \text{N} - \text{NO} \quad \text{H}_3\text{C} \quad \text{N} - \text{NH} \\
\text{O} & - \text{CH}_3 & \text{O} & - \text{CH}_3
\end{align*}
\]

We recently published the results of a thermochemical study of this reaction in the solid state by means of the DSC method [8, 9]. The present paper deals with the
influence of changes in the structure of the starting substance (I) on the kinetics of
the above reaction under isothermal and non-isothermal conditions.

Experimental

The derivatives of 1,3-dimethyl-4-alkylamino-5-nitrosouracil (I) (where alkyl
\( R = \text{CH}_3, \text{C}_2\text{H}_5, \text{i-so-C}_4\text{H}_9, (\text{CH}_2)_2\text{C}_6\text{H}_5, (\text{CH}_2)_2\text{OH}, \) and \((\text{CH}_2)_3\text{OH})\) were
prepared by nitrosation of I with propyl nitrite in methanol. The structures of the
prepared compounds were confirmed by spectral methods (UV, IR and \(^1\text{H} \text{NMR})\)
and elemental analysis. The isothermal and dynamic records (10 deg min
\(^{-1}\)) were
obtained with a DSC-2 calorimeter (Perkin-Elmer).

The measurements were carried out in nitrogen atmosphere, the flow rate being
20 cm\(^3\) min
\(^{-1}\). Indium and lead were used as standards for calibrating the
temperature.

Results and discussion

The kinetics of cyclocondensation reaction (I) was investigated for the six
different derivatives of I under isothermal and non-isothermal conditions (Table 1).
In both cases, we used kinetic functions in integral from (Table 2). These functions
are convenient for describing reactions in the solid state [1, 10].

Table 1 Temperatures and temperature interval used for isothermal and dynamic study of cyclo-
condensation reaction [1]

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound ( R )</th>
<th>Isothermal study ( T, K )</th>
<th>Non-isothermal study(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( \text{CH}_3 )</td>
<td>408, 410, 413, 415, 418</td>
<td>404, 423, 439</td>
<td></td>
</tr>
<tr>
<td>2 ( \text{C}_2\text{H}_5 )</td>
<td>375, 380, 385</td>
<td>369, 403, 416</td>
<td></td>
</tr>
<tr>
<td>3 ( \text{i-so-C}_4\text{H}_9 )</td>
<td>370, 375, 380</td>
<td>368, 391, 407</td>
<td></td>
</tr>
<tr>
<td>4 ((\text{CH}_2)_2\text{C}_6\text{H}_5 )</td>
<td>395, 400</td>
<td>390, 425, 432</td>
<td></td>
</tr>
<tr>
<td>5 ((\text{CH}_2)_2\text{OH} )</td>
<td>400, 405, 408, 410</td>
<td>399, 423, 431</td>
<td></td>
</tr>
<tr>
<td>6 ((\text{CH}_2)_3\text{OH} )</td>
<td>370, 373, 375, 378</td>
<td>365, 391, 406</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Heating rate was 10 deg min
\(^{-1}\)

\(^b\) \( T_i, T_p, T_f \) denote the initial, maximum and final temperatures of the DSC peak of the reaction,
respectively

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