

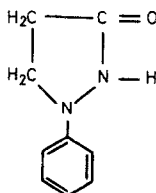
PYROLYSIS OF 1-PHENYL-3-PYRAZOLIDINONE

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Pyrolysis of 1-phenyl-3-pyrazolidinone (phenidone) was examined in static air atmosphere by the conventional dynamic heating technique in a derivatograph. The thermal stability of 1-phenyl-3-pyrazolidinone, its melting point and the kinetic parameters E , A and n of the first partial process of the pyrolysis at different heating rates were determined. It is shown that the thermal decomposition of 1-phenyl-3-pyrazolidinone in the presence of oxygen is a rather complicated process composed of several overlapping reactions. The pyrolysis is influenced by the conditions of thermal analysis.

1-Phenyl-3-pyrazolidinone (phenidone), $C_9H_{10}N_2O$ (I) is a white crystalline compound. Due to its strong reduction properties and some other specific qualities [1] it has found wide application in photography, chemical industry and medicine. 1-Phenyl-



-3-pyrazolidinone is widely applied as an effective stabilizing agent to many chemical compounds [1–5], an agent inhibiting corrosion [1] and an analytical reagent in chemical and medical laboratories [1] and it can be used to synthesize many chemical compounds [1, 6]. Lately, the complexes formed between 1-phenyl-3-pyrazolidinone and metal ions were investigated [7–10]. It has been found that various temperature conditions were needed to synthesize some of these complexes and it was necessary to know the thermal stability range of 1-phenyl-3-pyrazolidinone to analyse the thermal decomposition processes of these complexes.

Since the thermal decomposition of 1-phenyl-3-pyrazolidinone has not been investigated by researchers and only the effect of the moisture content on its flammability has been analysed [11], we undertook the task to determine the thermal stability range of this compound and investigated the effect of the heating rate on its decomposition in static air atmosphere.

Experimental

1-Phenyl-3-pyrazolidinone (pure) produced by Reachim (U. S. S. R.) was taken for the investigations. Examinations of the pyrolysis were carried out by means of a Derivatograph 1000/1500 °C of the Paulik–Paulik–Erdey system produced by the Hungarian Optical Works (MOM), Budapest. The recording device of the apparatus allowed to investigate simultaneously the mass change of the sample (TG), the rate of the mass change (DTG), the temperature of the sample (T) and the thermal changes that occurred in the sample (DTA), all vs. time (t). 500 mg samples of 1-phenyl-3-pyrazolidinone were used. The samples were placed in an open corundum crucible and were examined in the presence of air. $\alpha\text{-Al}_2\text{O}_3$ (corundum powder) was used as the reference inert substance. The simultaneous TG, DTG, DTA and T curves were recorded in the conventional way at a heating rate (β) of 20, 10, 5, 2.5, 1.25 and 0.6 deg \cdot min $^{-1}$. The investigations were carried out up to 1273 K, but when β was 0.6 deg \cdot min $^{-1}$ the sample could be heated only up to 773 K. The sensitivity of the balance was adjusted to 500 mg/100 divisions with the weighing accuracy $\pm 0.2\%$ for the TG curves. The rate of tape feed (u) on the recorder was 1, 2 or 5 mm/min and it was chosen in dependence of the succession of the partial processes of the pyrolysis on the DTG and DTA curves at different heating rates. We repeated every measurement in order to obtain information regarding the reproducibility of the curves.

Results and discussion

The thermoanalytical curves of the pyrolysis of 1-phenyl-3-pyrazolidinone recorded in the conventional way in the static air atmosphere are presented in Figs 1–3. Additional broken line DTG and DTG curves in these figures have been traced in from

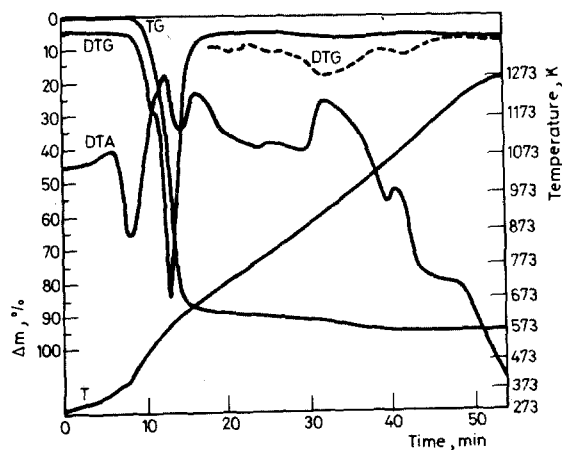


Fig. 1 Simultaneous TG, DTG, DTA and T curves of 1-phenyl-3-pyrazolidinone in static air atmosphere: $m_0 = 500$ mg, TG = 500 mg, DTG = 1/15, (--- DTG = 1/1), DTA = 1/5, $\beta = 20$ deg \cdot min $^{-1}$, $u = 5$ mm \cdot min $^{-1}$

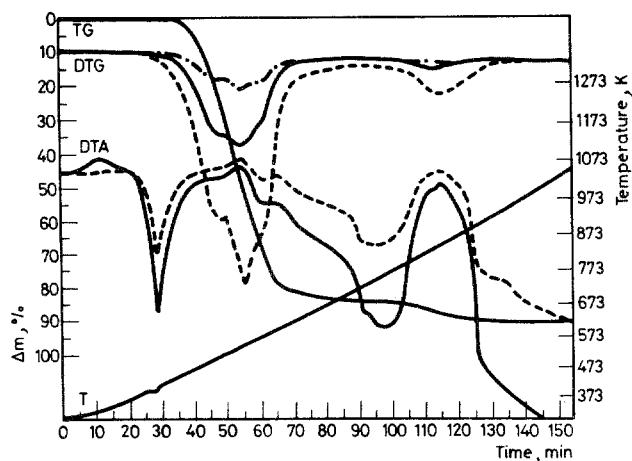


Fig. 2 Simultaneous TG, DTG, DTA and T curves of 1-phenyl-3-pyrazolidinone in static air atmosphere: $m_0 = 500$ mg, TG = 500 mg, DTG = 1/5, (--- DTG = 1/2), (-.-.- DTG = 1/15), DTA = 1/5, (--- DTA = 1/3), $\beta = 5 \text{ deg} \cdot \text{min}^{-1}$, $u = 2 \text{ mm} \cdot \text{min}^{-1}$

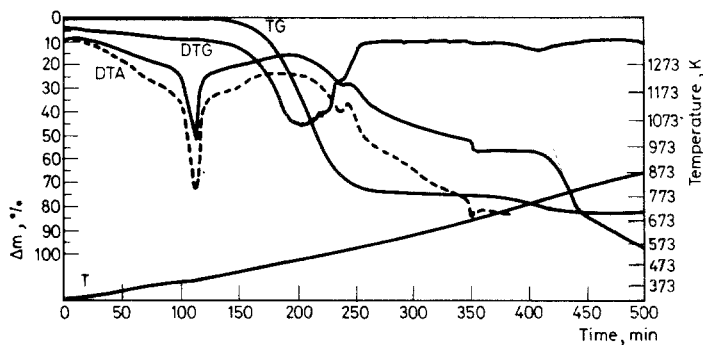


Fig. 3 Simultaneous TG, DTG, DTA and T curves of 1-phenyl-3-pyrazolidinone in static air atmosphere: $m_0 = 500$ mg, TG = 500 mg, DTG = 1/1, DTA = 1/2, (--- DTA = 1/1.5), $\beta = 1.25 \text{ deg} \cdot \text{min}^{-1}$, $u = 1 \text{ mm} \cdot \text{min}^{-1}$

some of the thermal curves which are not included in this work. These curves, recorded with different sensitivities of the galvanometers, allow for a better illustration of the pyrolysis of 1-phenyl-3-pyrazolidinone.

Table 1 presents the data that describe the thermal stability range of 1-phenyl-3-pyrazolidinone, its melting point and the first partial process of the pyrolysis, i.e. the decomposition of the compound.

1-Phenyl-3-pyrazolidinone is thermally stable up to 395 K. In the range of 393–398 K it melts and a distinct endothermic peak is observed on the DTA curve. The minimum of this endothermic peak determines the melting point of the compound [12]. The melting point at 394 K for $\beta = 1.25 \text{ deg} \cdot \text{min}^{-1}$ is identical with the literature data [1].

Table 1 Thermal stability, melting point and decomposition of 1-phenyl-3-pyrazolidinone as indicated by the thermoanalytical curves

| Properties and changes | Heating rate, β , deg \cdot min $^{-1}$ | | | | | |
|---|---|----------------|----------------|----------------|----------------|----------------|
| | 20 | 10 | 5 | 2.5 | 1.25 | 0.6 |
| Thermal stability range, K | to 418 | to 409 | to 396 | to 395 | to 399 | to 409 |
| Melting (the endothermic peak), K | 381 \div 493 | 389 \div 493 | 391 \div 463 | 393 \div 431 | 388 \div 409 | 386 \div 398 |
| Melting point, K | 421 | 411 | 402 | 399 | 394 | 391 |
| The rapid decomposition, K | 418 \div 672 | 409 \div 653 | 396 \div 627 | 395 \div 598 | 399 \div 568 | 409 \div 532 |
| Mass loss due to the rapid decomposition, % | 88.0 | 85.2 | 81.4 | 78.0 | 73.0 | 67.0 |
| The residue in the crucible that undergoes further decomposition, % | 12.0 | 14.8 | 18.6 | 22.0 | 27.0 | 33.0 |
| End of all the transformations, K | 1153 | 1023 | 933 | 873 | 813 | not determined |
| Total mass loss read from the TG curve, % | 95.0 | 92.8 | 90.8 | 87.0 | 83.0 | not determined |

When melted, 1-phenyl-3-pyrazolidinone undergoes decomposition, which is a rather complicated process. When the heating rates are high, the process is observed as a very rapid one (when β was 20 deg \cdot min $^{-1}$ we had to apply DTG = 1/15) and it is quite slow when $\beta = 0.6$ deg \cdot min $^{-1}$ (DTG = 1/1). Decomposition of 1-phenyl-3-pyrazolidinone takes place in a wide range of temperature. This range is the largest for $\beta = 20$ deg \cdot min $^{-1}$ and gets narrower when the heating rate is decreased.

The TG curves indicate (Figs 1–3) that the whole process of pyrolysis of 1-phenyl-3-pyrazolidinone is characterized mainly by two stages. These stages are very distinct on the TG curves and their complex character is proved by the DTG curves. The DTG curves indicate that the first stage, i.e. the initial decomposition of 1-phenyl-3-pyrazolidinone is composed of some partial processes. They are observed from about 400 K to 593 K when $\beta = 0.6$ deg \cdot min $^{-1}$ and to 769 K when $\beta = 20$ deg \cdot min $^{-1}$, and they are characterized by the loss of mass of 70 to 90%, respectively. When $\beta = 20$ deg \cdot min $^{-1}$ only two overlapping reactions can be observed on the DTG curves (Fig. 1) and the rate of the second one is higher (the maximum rate of decomposition $(dm/dt)_{\max}$ is observed at 591 K). On decreasing the heating rate a separation of overlapping reactions is observed and four peaks of the partial processes are indicated on the DTG curves. But when the heating rate is very low, i.e. $\beta = 0.6$ deg \cdot min $^{-1}$, the partial processes are observed as a single and a very flat, wide peak with only a slight inflexion on the DTG curve at $T = 497$ K.

When 1-phenyl-3-pyrazolidinone decomposes some thermal changes are observed

on the DTA curves, i.e. two exothermic changes (the height of the second peak is greater and the temperature of its maximum (T_p) exceeds 500 K) and one endothermic change followed by an intense exothermic reaction. The first two exothermic peaks are formed due to the degradation of 1-phenyl-3-pyrazolidinone while the endothermic peak is observed due to the evaporation of the decomposition products. The final exothermic peak is formed when some further decompositions of the substances remaining in the crucible take place. In spite of the endothermic changes on the DTA curves the total effect of all the partial processes is exothermic. When $\beta = 2.5 \text{ deg} \cdot \text{min}^{-1}$ and $1.25 \text{ deg} \cdot \text{min}^{-1}$ (Fig. 3) there appears on the DTA curves an additional third exothermic peak just before the endothermic one. When $\beta = 0.6 \text{ deg} \cdot \text{min}^{-1}$ two of the first exothermic changes are observed as one peak on the DTA curve.

This indicates that when the thermal decomposition of 1-phenyl-3-pyrazolidinone takes place in the static air atmosphere four overlapping exothermic processes occur and they are accompanied by an endothermic process of the evaporation of the decomposition products. The decomposition of 1-phenyl-3-pyrazolidinone is most probably bound with the opening of the pyrazolidinone ring and with the degradation of the phenyl ring. Furthermore, in the presence of oxygen, these reactions are most probably accompanied by some oxidation processes. A precise reaction scheme for the decomposition of 1-phenyl-3-pyrazolidinone will be determined after some further investigations carried on under inert gas atmosphere are performed together with the analysis of the decomposition products.

The different final mass loss of the samples (m_f) observed on the TG curves for the various heating rates was due to the deposition of the cooled down decomposition products of 1-phenyl-3-pyrazolidinone on the crucible holder. This problem will be solved during our further investigations where we plan to analyse also the effect of the amount of the sample on the thermal decomposition of 1-phenyl-3-pyrazolidinone.

When the rapid decomposition of 1-phenyl-3-pyrazolidinone is over, a slow mass loss on the TG curves can be observed due to further degradation of the decomposition products and weak exothermic peaks on the DTA curves. They can be well observed in Fig. 1. Finally, the last stage of the pyrolysis is observed on the thermo-analytical curves (Figs 1–3). This process is bound with a low mass loss (ca. 4–7% of the initial amount of the sample), and it is accompanied by two very strong overlapping exothermic-partial processes, what indicates that the combustion of the decomposition products of 1-phenyl-3-pyrazolidinone (which have remained in the crucible) takes place.

Table 2 tabulates the kinetic parameters E , A and n , i.e. the activation energy, the pre-exponential factor and the apparent reaction order of the first partial process of the decomposition of 1-phenyl-3-pyrazolidinone during heat treatment in static air atmosphere. The kinetic parameters were calculated by the method of Masłowska and co-workers [13–15]. Although the non-isothermal DTG curves point to the presence of more than one reaction (step) in the decomposition process, the consecutive reac-

Table 2 Kinetic parameters E , A and n of the first partial process of the decomposition of 1-phenyl-3-pyrazolidinone during heat treatment in static air atmosphere computed by the least square method for the different heating rates

| Heating rate, β , deg \cdot min $^{-1}$ | Kinetic parameters | | |
|--|---------------------------------|----------------------|-----|
| | E , kJ \cdot mol $^{-1}$ | A , s $^{-1}$ | n |
| 20 | 68.6 | $3.90 \cdot 10^8$ | 0.5 |
| 10 | 67.7 | $6.30 \cdot 10^8$ | 0.7 |
| 5 | 66.7 | $1.01 \cdot 10^9$ | 0.8 |
| 2.5 | 68.6 | $1.66 \cdot 10^9$ | 1.3 |
| 1.25 | 69.9 | $2.87 \cdot 10^9$ | 1.3 |
| 0.6 | 78.4 | $2.32 \cdot 10^{10}$ | 0.4 |

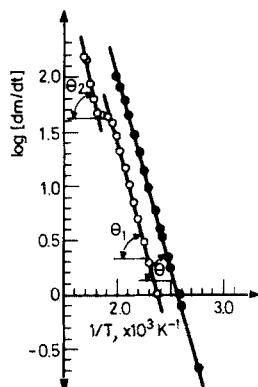


Fig. 4 Plots of $\log \frac{dm}{dt}$ vs. T^{-1} . $\circ\text{---}\circ$ $\beta = 20 \text{ deg} \cdot \text{min}^{-1}$ ($\text{DTG} = 1/15$), $\bullet\text{---}\bullet$ $\beta = 2.5 \text{ deg} \cdot \text{min}^{-1}$ ($\text{DTG} = 1/1$)

tions (steps) seem not to be completely superimposed on the first reaction. Therefore, it was possible to calculate the kinetic parameters for this process.

Linear graphs were plotted in coordinates $\log \left(\frac{dm}{dt} \right)$ vs. $\frac{1}{T}$, K^{-1} for all the curves obtained at different heating rates, as it is presented in Fig. 4 for the two values of β . The slopes of the straight lines thus obtained allowed to calculate the activation energy E by the equation:

$$E = -2.303 R \cdot \text{tg } \theta \quad (1)$$

where R is the gas constant. In fact, on the basis of the straight lines, points were selected to compute the activation energy by the least square method in accordance with the equation: $y = a + bx$, where $y = \log \left(\frac{dm}{dt} \right)$, $x = \frac{1}{T} \cdot 10^{-3}$, K^{-1} and

$b = -\frac{E}{2.303 R}$. The values of y and x were taken from figures such as Fig. 4 and the values of b were calculated for each of them. The value of b enabled calculation of the value of E with the equation (1). Constant activation energy values were observed for this stage of decomposition when $c \geq 0.92$ ($c = \frac{\Delta m_{\infty} - \Delta m}{\Delta m_{\infty}}$). Further, the linear plot of $\left[\log \left(\frac{dm}{dt} \right) + \frac{E}{RT} \log e \right]$ vs. $\log c$ was taken into consideration. The slopes of the straight lines thus obtained allowed to determine the apparent reaction order n and the intercepts on the ordinate gave the value of $\log A$. The least square computation method was next applied to the linear dependence. All the results are presented in Table 2.

Conclusions

1. The analysis of the thermal decomposition of 1-phenyl-3-pyrazolidinone at different heating rates β allowed to determine its thermal stability range, to analyse the stages of its decomposition in the static air atmosphere, to determine the thermal processes that were not distinct on all the DTA curves at some of the heating rates and, therefore, to reveal the presence of several steps in the process under consideration.

2. 1-Phenyl-3-pyrazolidinone is thermally stable up to 395 K.

3. The rates of the partial processes of the pyrolysis of 1-phenyl-3-pyrazolidinone depend on the heating rate β and are the highest when $\beta = 20 \text{ deg} \cdot \text{min}^{-1}$.

4. The positions of the peaks on the DTG and DTA curves are also heating rate dependent and the shift in T_p toward lower temperatures is observed when β is decreased.

5. The melting point 394 K read for the heating rate $\beta = 1.25 \text{ deg} \cdot \text{min}^{-1}$ is identical to the literature data [1].

6. The thermal decomposition of 1-phenyl-3-pyrazolidinone takes place in a wide temperature interval (above 395 K) and is characterized by a total exothermic effect. It is bound with the opening of the pyrazolidinone ring and the degradation of the phenyl ring.

7. The thermal decomposition of 1-phenyl-3-pyrazolidinone in the presence of oxygen is a rather complicated process composed of four overlapping exothermic reactions accompanied by the endothermic process of evaporation of the decomposition products.

8. The total mass loss observed for this decomposition exceeds 70% and it is heating rate dependent.

9. In the final stage of the pyrolysis of 1-phenyl-3-pyrazolidinone the combustion of the decomposition products that have remained in the crucible takes place and very high exothermic peaks are observed on the DTA curves, but the process is accompanied by a low mass loss.

10. The values of the kinetic parameters E , A and n indicate that when 1-phenyl-3-pyrazolidinone is heated in the presence of oxygen at very low heating rates ($\beta = 0.6 \text{ deg} \cdot \text{min}^{-1}$) then its oxidation occurs and a new substance is formed in the crucible.

References

- 1 M. E. Guzek and J. Masłowska, *Zeszyty Naukowe PŁ, Technologia i Chemia Spożywcza* (Sci. Bull. of Łódź Techn. Univ., Production Technology and Food Chemistry), 38 (431) (1984) 53.
- 2 C. E. Tholstrup, USA patent 2.808.417 (1957); *Chem. Abs.*, 52:761f.
- 3 J. Masłowska, Pol. patent applied, 1981.
- 4 Československý Lekopis, Státní Zdravotnické Nakl., 3rd Edition, Praha, 1970, p.412.
- 5 J. Masłowska, W. Krakowiak and J. Duda, *Farm. Pol.*, 37 (8) (1981) 449.
- 6 H. Dorn, A. Otto and H. Dilcher, German (DDR) patent 84.014, Aug. 20, 1971; *Chem. Abs.*, 78:72132c.
- 7 A. Fabrikanos, G. Pallikaris and V. Havredaki, *Chem. Ind. (London)*, 6 (1975) 281.
- 8 J. Masłowska and M. E. Guzek, A Study of Reaction Equilibria in 1-Phenyl-3-Pyrazolidinone - Ionic Transition Metals Systems. Presented at the XXII. International Conference on Coordination Chemistry, August 23-27, 1982, Budapest, Hungary.
- 9 J. Masłowska and M. E. Guzek, Paper Electrophoresis Investigations of Complexes Formed between 1-Phenyl-3-Pyrazolidinone and Metal Ions (in Polish). Presented at the Conference organized by P. T. Ch. and SITPCChem., September 22-25, 1982, Lublin (Poland), Part A, p. 57.
- 10 J. Masłowska and M. E. Guzek, *Chromatographia*, 17 (8) (1983) 426.
- 11 M. N. Cwietkow, A. J. Korolczenko, A. W. Iwanow, W. J. Jaszin and W. P. Bubajew, *Chim.-Farm. Żurnal*, 11 (8) (1977) 74.
- 12 L. Erdey, *Gravimetric Analysis*, Pergamon Press, Oxford, 1965.
- 13 J. Masłowska, J. B. Baranowski, E. Łodyga-Chruścińska, A. Baranowska and K. Marszał, *Zeszyty Naukowe PŁ, Technologia i Chemia Spożywcza* (Sci. Bull. of Łódź Techn. Univ., Production Technology and Food Chemistry), 35 (361) (1980) 321.
- 14 J. Masłowska and R. Krupa, *Zeszyty Naukowe PŁ, Technologia i Chemia Spożywcza* (Sci. Bull. of Łódź Techn. Univ., Production Technology and Food Chemistry), 39 (1983) 24.
- 15 J. Masłowska and A. Baranowska, *J. Thermal Anal.*, 29 (1984) 309.

Zusammenfassung — Die Pyrolyse von 1-Phenyl-3-pyrazolidinon (Phenidon) wurde mit einem Derivatographen in einer statischen Luftatmosphäre und bei konventioneller dynamischer Aufheizung untersucht. Die thermische Stabilität und der Schmelzpunkt von 1-Phenyl-3-pyrazolidinon sowie die kinetischen Parameter E , A und n des ersten Teilprozesses der Pyrolyse für verschiedene Aufheizesgeschwindigkeiten wurden bestimmt. Es stellte sich heraus, daß die in Gegenwart von Sauerstoff verlaufende thermische Zersetzung von 1-Phenyl-3-pyrazolidinon ein ziemlich komplizierter, aus mehreren sich überlappenden Teilschritten bestehender Prozeß ist. Die Pyrolyse wird durch die Bedingungen der thermischen Analyse beeinflußt.

Резюме — Пиролиз 1-фенил-3-пиразолидинона (фенидона) был исследован с помощью дериватографа в статической атмосфере воздуха при обычном динамическом нагреве. Определены термостойкость соединения, его точка плавления и кинетические параметры E , A и n для первого частичного процесса пиролиза, проведенного при различных скоростях нагрева. Установлено, что термическое разложение 1-фенил-3-пиразолидинона в присутствии кислорода является сложным процессом, состоящим из нескольких перекрывающихся реакций. Процесс пиролиза затрагивается условиями термического анализа.