# INVESTIGATION OF THERMAL STABILITY OF SOME NITROAROMATIC DERIVATIVES BY DSC

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The thermal behaviour of several *mono* and *di*-nitroaromatic compounds (*o*, *m* and *p*-nitrophenols, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,3-dinitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and 2,4-dinitrophenylhydrazine (DNPH)) was examined using the DSC method at ambient pressure in an argon atmosphere. Except for DNPH, all investigated compounds melted and evaporated without decomposition. For linear heating, DNPH showed an exothermic decomposition following its melting. The exothermic decomposition was also detected in isothermal conditions at temperatures lower than the melting point. A runaway decomposition of DNPH using larger samples was also studied using a Lütolf oven.

## 1. Introduction

The hazards connected with the exothermic decomposition of condensed chemicals are often not well understood and sometimes wrongly estimated [1,2]. The reason is that these reactions are influenced by very different material properties like purity, crystallization form, granulation, quantity etc. Thermal runaway occurs when large quantities of such substances are operated in adiabatic or quasi-adiabatic conditions. The heat effect of decomposition is one of the most important characteristic parameters necessary for the evaluation of hazards of these chemicals. The corresponding reaction heat can be measured using specific thermal methods. Among all these methods the most common are simultaneous thermal analysis (STA) [3], differential scanning calorimetry (DSC) [4,5], which use very small samples, and accelerating rate calorimetry (ARC) [1]. Although these methods are useful for measurements of the reaction energy of decomposition and other thermodynamic and kinetic properties, the runaway conditions can be reached only for larger samples. A specific device for safety study is the Lütolf oven, operated either isothermally or non-isothermally [6,7]. The experimental measurements allow the identification of exothermic decompositions and the evaluation of the heat of reaction and, according to an accepted kinetic model, of the overall activation energy.

The number of compounds able of exothermic decompositions is very large. The nitro-derivatives constitute a very important class frequently encountered in chemical industry and in different laboratories. Their runaway behaviour is strongly dependent on the specific conditions, especially on pressure regime. For closed systems, when the pressure increases during decomposition, many nitro-derivatives lead to explosive decomposition after their melting. At normal pressure the corresponding liquids are more stable justifying the interest for further investigation of these compounds.

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The most efficient method for screening the exothermic behaviour of different condensed compounds is DSC [4]. This method requires a small sample size and a short analysis time. The area of the peak is proportional to the energy of the exothermic or endothermic effects. In the dynamic mode (temperature programmed experiments) a quick overview of the entire temperature range of interest is obtained. The observed initial temperature of exothermic response allows a preliminary estimate of the temperature range in which the undesired reaction could occur. From the analysis of exothermic peak the heat of reaction and the partial heats of reaction at different conversions can be obtained. Several other characteristics like the melting point, the melting heat, induction period and the activation energy of explosive decomposition can also be determined from the same curves. Isothermal measurements in the region of the onset temperature of the exothermic peak usually clarify whether or not decomposition occurs by an autocatalytic mechanism [8].

## 2. Experimental

The thermal stabilities of the following substances: *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 2,3-dinitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenylhydrazine (DNPH) have been evaluated at normal pressure. All chemicals were of reagent grade (Aldrich, Merck, Serva, BDH, Reanal).

A Cahn model DSC 550 differential scanning calorimeter was used for the evaluation of the thermal decomposition of nitro aromatic compounds in both linear heating and isothermal conditions. Runs with linear heating were performed within the temperature range 25 to $300^0$C, at a heating rate of $10^0$C min$^{-1}$ on approximately 1 mg of sample. The isothermal decomposition of DNPH was followed using the same heating rate up to a temperature lower than the melting point. The exothermic decomposition peak appeared after a characteristic induction period. The samples were tested in sealed aluminium crucibles with a pinhole in the lid to prevent pressure build up in the crucible during the decomposition. All experiments were carried out under argon atmosphere.

The Lütolf method was also used for evaluating the thermal runaway conditions of DNPH [6]. The Lütolf apparatus is an electrically heated aluminium block with holes for 6 test tubes and is provided with temperature control for different heating programs and two thermocouples for recording reference and sample temperatures. The tests consisted in heating 2g of sample and 2g of reference (graphite) in open test tubes, from ambient temperature up to $350^0$C with a heating rate of $2.5^0$C min$^{-1}$. For DNPH, a 2g sample resulted in a violent decomposition with loss of substance from the test tube. The tests were then performed on DNPH samples diluted with an inert solid (glass spheres of fine granulation, 80/100 mesh) in weight ratios of 1:2 or 1:3.

## 3. Results & Discussion

When DSC method at normal pressure was used it was found that all investigated mono and dinitrophenols and dinitrobenzene compounds melted without thermal decomposition. No solid residue was found in the pans at the end of the run. The thermal characteristic data of these compounds were determined from DSC thermograms (melting points, taken as the

minimum of the endothermic peak, and melting heats) and the results were compared with literature data. A representative thermogram for 2,6-dinitrophenol is given in Fig. 1.
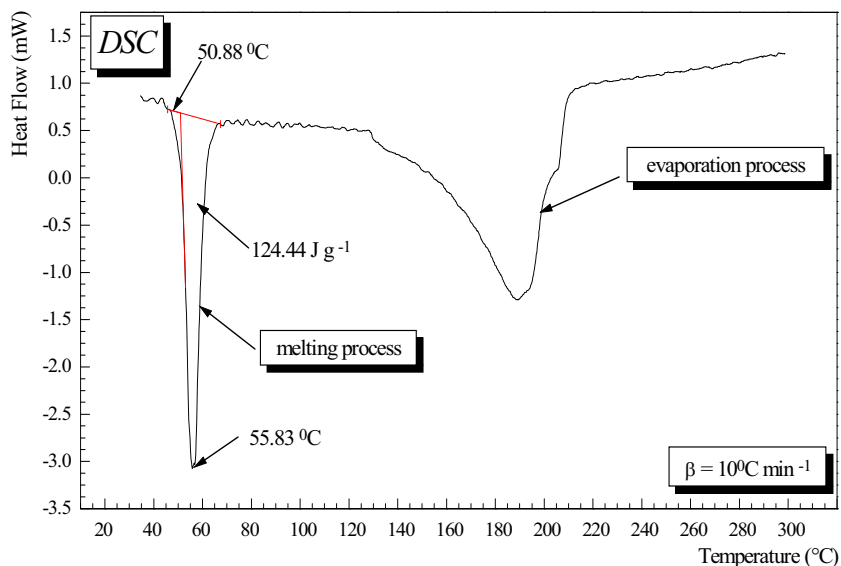


Fig. 1: *The thermogram for 2,6-dinitrophenol.*

After the melting process with the peak temperature $55.83^0C$ and with the melting heat $124.44$ J $g^{-1}$ the next endothermic process represents the evaporation. Its form indicates the existence of two processes, the last one being associated with the desorption of the sample from the metal surface.

The characteristic properties of these compounds are listed in Table 1.

**Table 1. Melting points and melting heats of analysed compounds**

| No | Compound | mp $^0$C (literature) | mp $^0$C (measured) | $\Delta H$ m (J g$^{-1}$) | Exothermic decomposition |
|----|----------|------------------------|----------------------|----------------------------|--------------------------|
| 1 | *o*-nitrophenol | 44.80 | 43.06 | 122.55 | – |
| 2 | *m*-nitrophenol | 96.80 | 95.80 | 129.82 | – |
| 3 | *p*-nitrophenol | 113.80 | 113.19 | 79.05 | – |
| 4 | 2,3-dinitrophenol | 144.50 | 145.80 | 123.12 | – |
| 5 | 2,4-dinitrophenol | 115.50 | 110.00 | 142.25 | – |
| 6 | 2,6-dinitrophenol | 63.50 | 55.83 | 124.44 | – |
| 7 | 1,3-dinitrobenzene | 90.00 | 87.24 | 117.09 | – |
| 8 | 1,4-dinitrobenzene | 174.00 | 172.76 | 104.55 | – |
| 9 | 2,4-dinitrophenylhydrazine | 198.14 | 200.91 | 95.34 | + |

DNPH has a different behaviour. Under DSC linear heating it shows a melting peak at $200^0C$, which is immediately followed by the exothermic decomposition between 210 and $230^0C$. A typical result is shown in Fig. 2 for a heating rate of $10^0C$ min$^{-1}$.
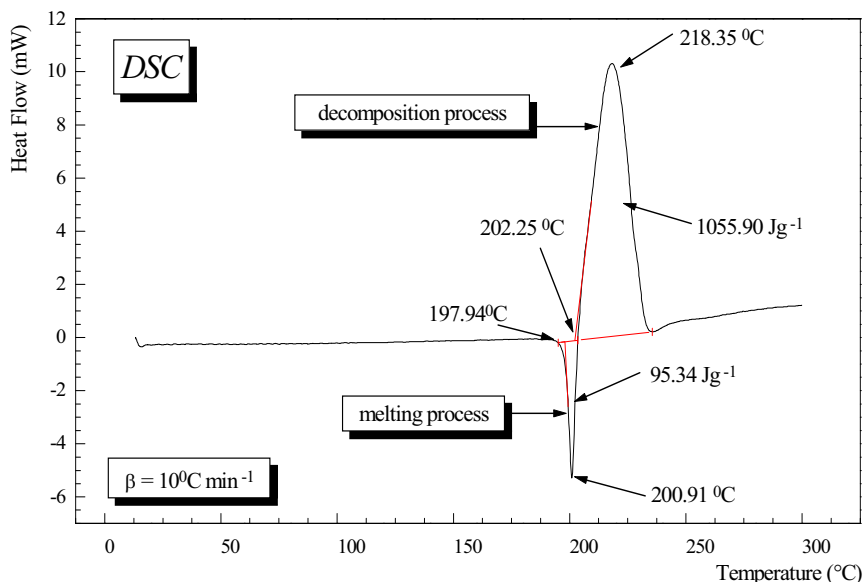
Fig. 2: *The thermogram of DNPH for linear heating regime.*

It can be observed that the melting and the beginning of the decomposition are partially superposed. The decomposition process in this case occurs in liquid phase. The corresponding heats of melting and decomposition were evaluated neglecting this superposition. Further information on this exothermic decomposition can be obtained from isothermal experiments. A typical result is given in Fig. 3.
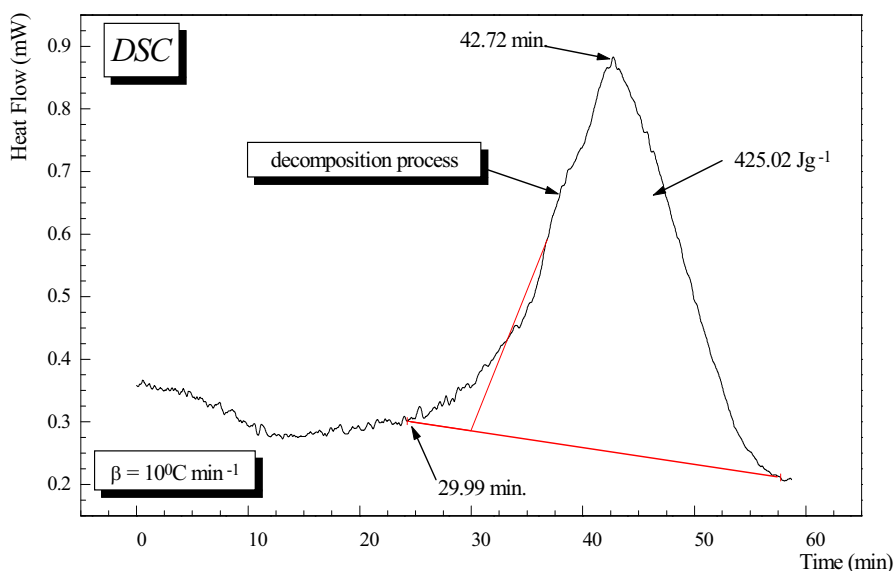


Fig. 3: *The thermogram of DNPH for isothermal regime.*

The reaction energy is much lower in isothermal experiments as compared with linear heating measurements. The difference can be assigned to endothermic melting and evaporation processes.

The Lütolf test of DNPH under temperature-programmed conditions indicates a violent exothermic reaction, without apparent melting. The Lütolf thermogram of DNPH diluted with glass spheres (1:3 weight ratio) is shown in Fig. 4. Under these conditions, the onset temperature of decomposition was $196^{0}C$ and the maximum rate of decomposition was observed at $266^{0}C$.
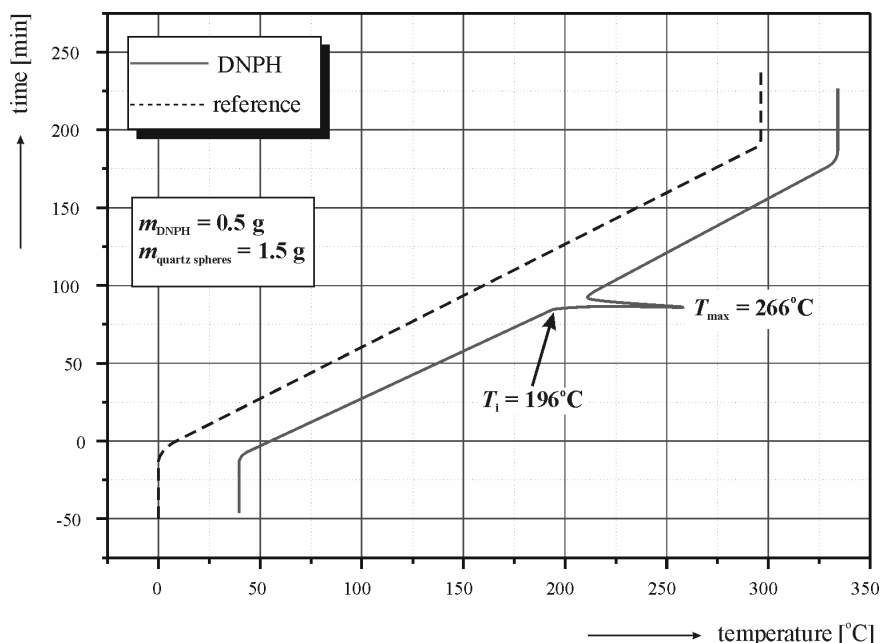


Fig. 4: *Lütolf thermogram of DNPH diluted with glass spheres.*

The characteristic temperature corresponding to the maximum decomposition rate evaluated from the Lütolf thermogram is higher by about $48^{0}C$ than the corresponding value evaluated from DSC thermogram. This displacement might arise from the different transfer rate between the sample and the temperature sensor, which is sample mass dependent, and from the different time constants of the thermocouples.

## Conclusions

The analysis of the DSC thermograms indicates that the following compounds: *o, m, p*-nitrophenols, 1,3 and 1,4-dinitrobenzenes, 2,3, 2,4 and 2,6-dinitrophenols are thermally stable at constant ambient pressure between 25 and $300^{0}C$, although they are potentially explosive. This behaviour is different from other reported data [1] referring to exothermic decomposition during **isochoric** or **adiabatic** heating of some of these compounds (1,3-dinitrobenzene, 3 and 4-nitrophenols).

At constant pressure DNPH decomposes exothermically either for linear heating, following its melting, or for isothermal regime starting at temperatures lower than the melting point. For larger samples, used in a Lütolf type experiment, DNPH exhibits a runaway decomposition.

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