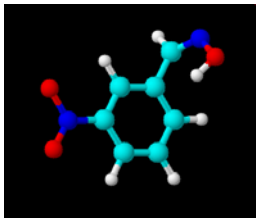
Rapid Screening Device - RSD™
Technical Application Note 104
Sample Data: 3 Nitrobenzaldoxime

Introduction

3 Nitrobenzaldoxime is well used reagent synthesized by many specialist chemical manufacturers. It has a melting point at 120°C. The Structure is shown below. The nitro group and the conjugated carbon nitrogen double bond strongly suggest that this reagent will decompose exothermcially. However its stability and effect of impurity on stability have caused concern for users of this reagent.



The RSD is a rapid and reliable method to screen any chemical to see thermal and pressure effects and thus will quickly screen any new reagent for all decomposition hazards and is likely to discriminate between samples from different manufacturers if small amounts of impurities (other nitro containing compounds) can cause significant decrease in stability.

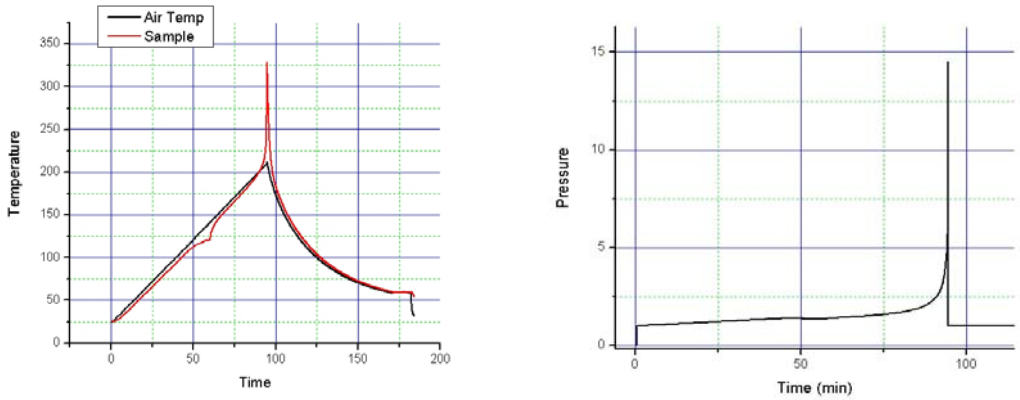
Experimental

A pure sample of 2.60 grams was placed in a metal pressure tight sample container and no reference was used. The local air temperature outside the sample/container was used as the control temperature and this with ambient pressure was used as 'reference' in data analysis. A heating rate of 2°C/min was used. This is somewhat lower than used for screening but is a heating rate used in other apparatus, notably the Carius Tube. The ramp was set to 400°C with a safety pressure limit of 40 bar (controlled with a burst disc).

Results

The test proceeded according to the program but near 200°C there was uncontrolled exothermic reaction. The pressure exceeded 40 bar and the burst disk ruptured. The test terminated as the rapid change in condition exceeded two of the safety cut-out conditions imposed.

The results showed a major endotherm due to melting of the sample at 120°C. Above 170°C the exothermic decomposition commences and this accelerates with temperature until the mechanism change to a self heating decomposition to an explosive branch propagating mechanism.



Temperature and Pressure data plotted against Time

thermal hazard technology

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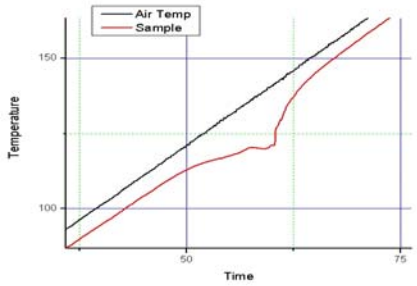
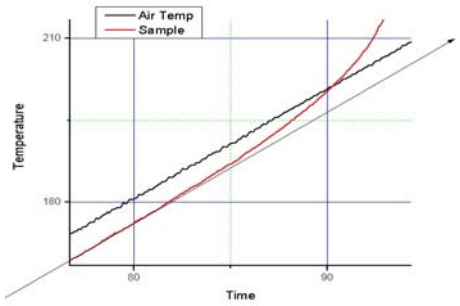
Discussion and Conclusions

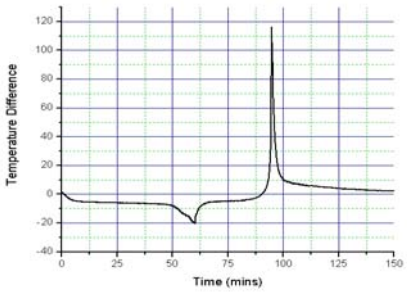
The graphs shown overleaf illustrate raw data from the RSD. The temperature and pressure data together indicate simply the melting and the decomposition. In this pure sample there is no indication of other reactions. Below the two graphs are zoom plots of the temperature against time data.

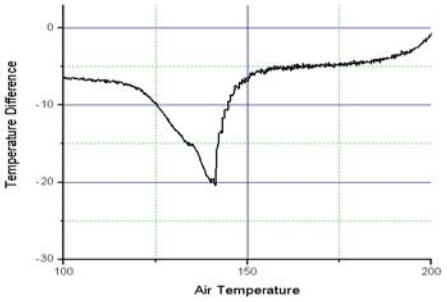




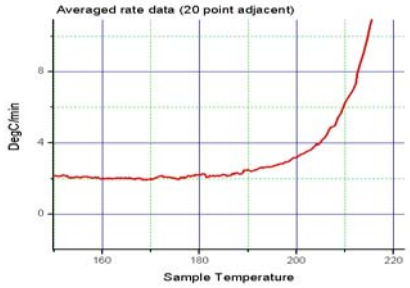
The graphs highlight the melting endotherm and the decomposition exotherm.

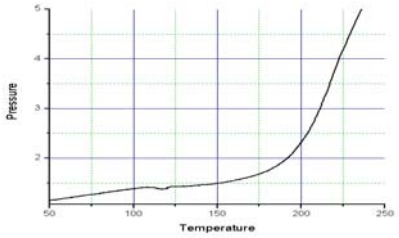
There was no reference with this test—but the two plots below shows temperature difference between sample and the air control temperature that may be used as a reference.





The temperature difference between the air and the sample is not zero but close to –6ºC under these conditions. The plot above has been zoomed to illustrate the onset of exothermic reaction, clearly close to 170ºC. The onset seen from a derivative temperature plot is not precise. The plots shown below indicates onset near 180ºC.





Pressure data plotted against temperature is also a good indicator of reaction—here without any solvent in the sample a reference is less relevant. Note the discontinuity at the melting. The graph shown above indicates the pressure rise and shows onset near 160°C, 10°C lower than the thermal data.

The results from this sample indicate that pure 3-nitrobenzaldoxime will from 160°C and this reaction may be explosive. Here is a good example where the pressure data is of significant help.