Rapid Screening Device - RSD™
Technical Application Note 17
Effect of Impurity or Catalysis: Multiple Sample Analysis

Introduction

The safety of scaled-up chemical reactions often can be simply and reliably qualified by calorimetry and other methods. However, incidents occur when upset conditions or unusual scenarios occur.

As such, it is advisable to consider as part of any safety program not just the expected or usual but situations that may arise. These may be upset conditions, incorrect reagent quantity or the ingress of foreign matter. The Bhopal tragedy was caused by water ingress into a reaction that although dangerous itself was well understood and simply controlled.

The RSD offers the possibility to test multiple samples and thus in one test it is possible to determine the heat and gas release that will occur from a reaction mixture and from reaction mixtures modified to simulate credible upset scenarios.

To simply illustrate such a case here, data from a test of Peroxide A in solution of ethyl benzene is given. The effect of sample holder (metal or glass) illustration catalytic effect of metal.

Conditions

Three samples were used. All were housed in a 're-useable screw-top sample holder' with an insert capable of holding 2 grams of sample. The samples were; solvent using a 9 mm glass insert, sample with peroxide using a 9 mm glass insert, sample with peroxide using a 9 mm stainless steel insert. In the glass insert sample, the thermocouple itself was housed in a capillary melting point tube. As such, this sample was not in contact with any metal. A 5°C/min heating rate was used. 160 bar pressure transducers were used.

Results

In Fig 1 and Fig 2 below, the red trace is the peroxide only in contact with glass; the green traces is the peroxide in the sample in contact with metal; the light blue trace is the 'reference' solvent-only sample and the dark blue temperature trace.

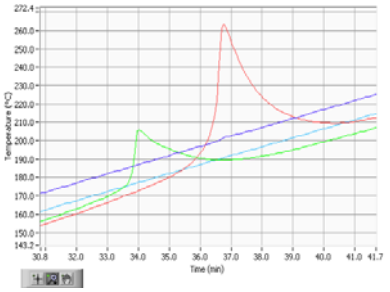

Fig 1

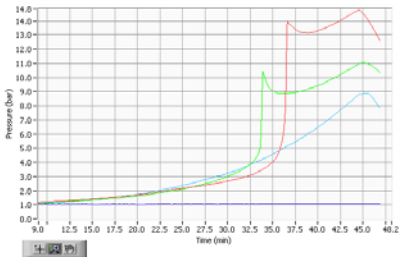

Fig 2

The three figures below (Fig 3 — Fig 5) indicate the peroxide sample in contact with glass data subtracted from the solvent sample. Onset of exothermic reaction (as observed from the middle graph) is near 150°C and the sample reacts very rapidly near 190°C. Pressure data is shown but not discussed. This would require normalisation to obtain gas release information.

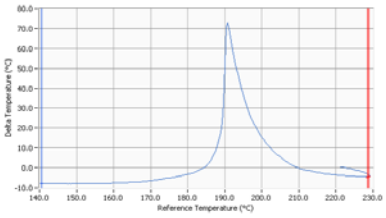

Fig 3

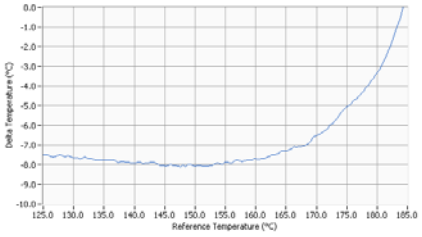

Fig 4

thermal hazard technology

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Fig 5

The three figures (Fig 6 — Fig 8) below indicate the peroxide sample in contact with metal data subtracted from the solvent sample. Onset of exothermic reaction (again as observed from the middle graph) is near 135°C and the sample reacts violently near 175°C. Pressure data again is shown but not discussed.

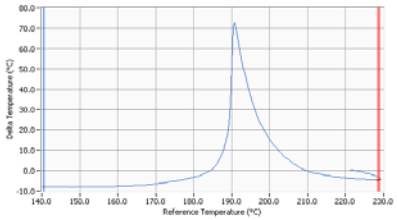

Fig 6

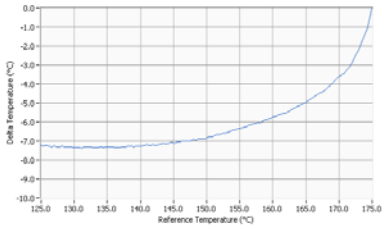

Fig 7

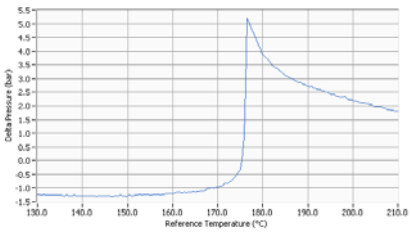

Fig 8

In the final graph (Fig 9) the peroxide sample in contact with glass has been selected as the 'reference' and from this data the data from the peroxide sample in contact with metal has been subtracted.

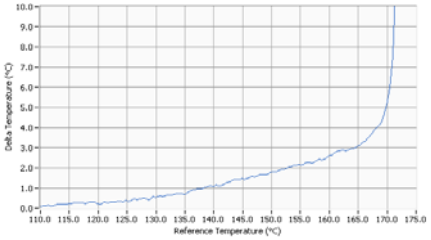

Fig 9

Discussion and Conclusions

Clearly the effect of metal catalysing the reaction is easily seen. The onset temperature is lowered by 15—20°C. In addition, though not initially obvious, it can be seen that the sample metal catalysed reacts more rapidly than the sample in glass. This confirms the view that there is autocatalytic reaction when catalysed. It is also clear that the sample in contact with metal gave a recorded heat release much lower than the sample in contact with glass. That the heat release from the sample in contact with glass was that expected from the decomposition. The reason a low heat release is recorded with the sample in contact with metal can be explained simply; the sample holder allows sample to be ejected from the insert into the main body of the re-useable sample holder.

Comparison of the two peroxides gives the most sensitive analysis. Here the difference between sample is observed from 125°C.

The RSD can be seen from this simple example to be a tool to evaluate many reaction scenarios rapid and quantative such evaluation can be carried out reliably and without significant expense, the consumable cost being only disposable inserts.