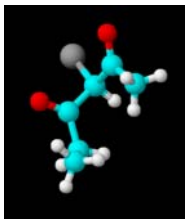
Rapid Screening Device - RSD™
Technical Application Note 105
Sample Data: Ethyl 2 Chloroacetoacetate

Introduction

Ethyl-2-chloroacetoacetate is an internediate widely used in addtion reqactions for chemical synthesis. Little is know of its decomposition behavious other than there has been noticed that significant pressure is generated.



The RSD is a rapid and reliable method to screen any chemical to see thermal and pressure effects and thus will quickly screen such a reagent for any decomposition hazards

Experimental

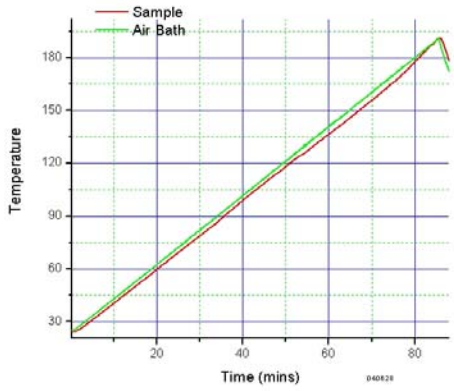
A sample of 1.53 grams was placed in a metal pressure tight sample tube container and no reference was used. The local air temperature outside the sample/container was used as the control temperature and this with ambient pressure was used as 'reference' in data analysis. A heating rate of 2°C/min was 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 300°C with a safety pressure limit of 40 bar was set—above this pressure rapid air cooling would occur and the test would terminate.

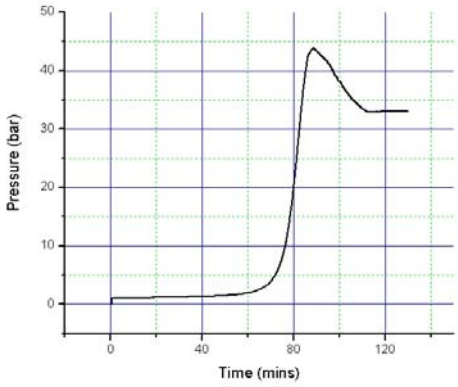
Results

The test proceeded according to the program but near 190°C the pressure exceeded 40 bar and the test terminated.

The results showed a broad very shallow exotherm in the temperature range 90-130°C and above 160°C a further exotherm commenced. However there appears to be no pressure rise associated with the first exotherm but large pressure rise associated with the second exotherm.

Upon cooling the pressure falls—as a pressure limit was set for cut out and not a burst disc, the final pressure upon cooling is also seen





Temperature and Pressure data plotted against Time

thermal hazard technology

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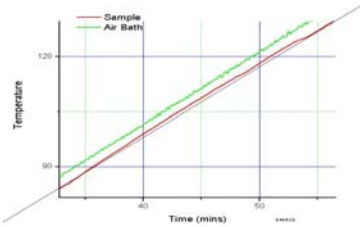
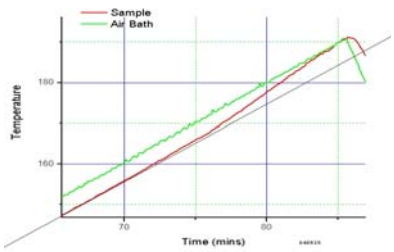
Discussion and Conclusions

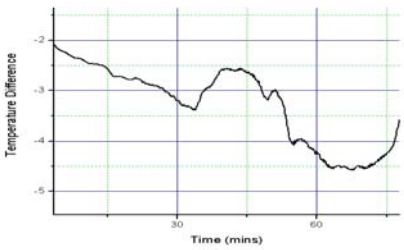
The graphs shown overleaf illustrate raw data from the RSD the pressure rise is clear, the temperature events are less clearly visible. Below the two graphs are zoom plots of the temperature against time data.

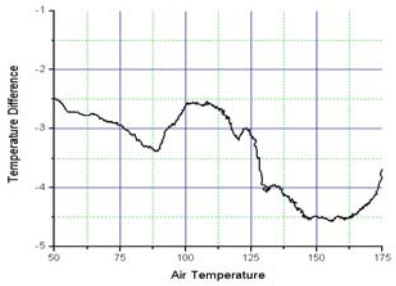




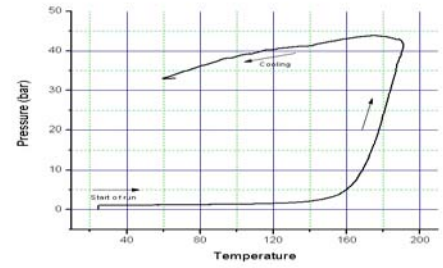
The upper plot shows the small exotherm, this might be due to impurity reaction. The lower graph illustrates the start of the main decomposition reaction.

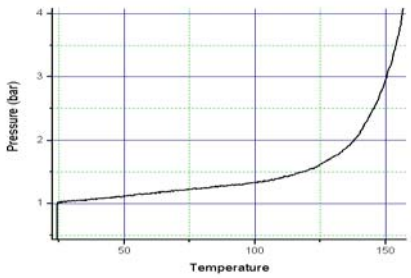
There was no reference with this test—but the two plots below shows temperature difference between sample and the air control temperature that may be used as a reference. The sensitivity is high and thus the pressure difference variation with temperature is significant (ie the baseline slopes. However the lower temperature initial exotherm is clearly seen as is the onset of the major decomposition.





The pressure data is also valuable in determining low energy and onset of transitions. This is plotted without subtraction of a reference and thus there is continued increase in pressure. Here is a good example of how when the temperature data is of low energy and not ideal the pressure data can give precise onset information. Onset is seen just above 100°C.





With low energy peaks recorded in this test derivative plots would be of little use. However a test that would terminate at a higher pressure may give more information on the main exothermic decomposition reaction.