Vessel Pressure Relief

Discharges

Pressure rise during homogeneous decomposition and deflagration

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Only a small part of the non-explosive substances are deflagrable. But a number of incidents have been caused by their deflagration. We have measured the temperature-time curves of the deflagration of some of these substances in a closed vessel. The rate of pressure increase was to a first approximation proportional to the pressure, except for one substance where it was proportional to a higher power of pressure. The pressure-time-curves of homogeneous decomposition were also measured but were more complicated than the results of the deflagration measurements.

Keywords:- pressure rise, homogeneous decomposition, deflagration,

The progressive exothermic decomposition of substances, commonly known as "deflagration", has frequently led to unpleasant incidents in the chemical industry. While it is true that only a small proportion of the substances produced are capable of deflagration, for the few that are the probability of its occurrence is especially large.

Deflagration is a familiar process in rocket fuels and explosives. In these cases the process is usually rapid and can easily become a detonation. Here we wish to consider slow deflagration which can appear in certain chemical compounds as an undesirable occurrence. These substances are usually not capable of detonation.

The following table lists some of these substances that are capable of deflagration and shows their deflagration rates [cf. 1].

Table 1: Deflagrable substances

Substances	Deflagration rate (cm/min)
4-Nitrosophenol	8
1-Nitrosonaphthol-(2)	0.74
Hydroxylammonium sulfate	5.6
Ammonium dichromate	2.2
Sodium-3-nitrobenzene sulfonate	4.5
Diphenyltriazene	2.0
Pigment orange CI 12075	1.8

The deflagration rates listed were measured from the top surface downward. The substances were placed in a 100 to 150 cm^3 glass beaker with a diameter of about 5 cm and ignited at the top with an ignition mixutre consisting of Si and PbO$_2$ in the ratio 2 : 1. After ignition the deflagration proceeded uniformly and was timed with a stopwatch.

Table 2 lists some mixtures that are deflagrable.

Table 2: Deflagrable mixtures

Mixture with m/m ratio	Deflagration rate (cm/min)
4-Chloronitrobenzene + KOH (1 : 1.5)	1.3
4-Nitrobenzoic acid + KOH (1 : 2)	5.1
4-Nitrophenol + KOH (1 : 1.5)	30
2-Nitrobenzaldehyde + activated charcoal (1.5 : 1)	1.25

Although most mononitro compounds are not deflagrable, their mixtures with potassium hydroxide or sodium hydroxide will deflagrate readily.

Here we will report on the deflagration of solid powders. During deflagration some of the substances pass through the liquid state. Liquid substances and mixtures of liquid substances can also deflagrate, but by a different mechanism. In loose powder the heat transfer is by convection of the generated gas within the unburnt powder. When liquids deflagrate a flame zone forms on the liquid, in which the substance vaporizes and deflagrates.

The objective of the present studies was to determine the pressure rise during deflagration in a closed vessel. We have made no effort to keep the pressure constant but allowed the rising pressure to act on the deflagration. According to the prevailing theory [2] the deflagration rate will increase sharply with rising pressure. It was our intention to compare the pressure rise occurring during deflagration with that resulting from homogeneous decomposition. It was found, however, that the pressure rise during deflagration is relatively easy to interpret but not that occurring during homogeneous decomposition.

Experimental arrangement

The experiments to study homogeneous decomposition and deflagration were conducted in the same apparatus. Suitable apparatus to study deflagration can be found in the literature [3, 4]. The design of the apparatus for studying homogeneous decomposition has already been published by the authors [5]. It is shown schematically in Fig. 1.

The autoclave with a 200 cm^3 capacity (Nova) will withstand pressures of 700 or 2000 bars. The substance is placed in a glass container that fits exactly into the autoclave. A wire coil is built into the autoclave for ignition in the deflagration studies. The wire dips into the ignition mixture of Si and PbO$_2$ (mixing ratio 2 : 1) with which the deflagration is ignited uniformly from the top surface. The Si-PbO$_2$ mixture was introduced by Gibson for ignition in the fire train test [6].

In the deflagration studies the autoclave was at room temperature; for the study of "homogeneous" decomposition without a source of ignition it was slowly heated in an oven. In both cases the same arrangement was used for pressure measurement, consisting of a piezo-resistive pressure transducer, a transient recorder and a graphic recorder. The transient recorder was especially important for the homogeneous decomposition trials because it was not known initially when the pressure rise would begin.

There is reason to doubt that the trials without an igniter really did proceed homogeneously. With regard to the substances that were fluid at the time of decomposition, we believe that homogeneous decomposition occurred; this can also be inferred from the pressure-time curves. For the substances that remained solid up to the end such as ammonium dichromate it is difficult to exclude the possibility of a temperature gradient during heating, and it is possible that the last stage of decomposition was deflagration.

Results

Figs. 2 to 5 show the pressure-time curves measured for homogeneous decompositon. These graphs can be divided into two different types. For some of the substances the inflection point is attained soon after the start of pressure rise (diphenyltriazene, 2-nitrobenzaldehyde). The shape of this pressure-time curve is at first incomprehensible. According to the theory of thermal explosion the reaction rate and hence also the rate of pressure rise should increase over a wide range. But it must be recalled that during decomposition the substance vaporizes and attains a supercritical state. In consequence it is easily possible that the decomposition process will slow down, as is observed.

For other substances the rate of pressure rise increases almost to the end and attains its maximum rather late (ammonium dichromate, azoisobutyronitrile). At least in the case of ammonium dichromate, which does not vaporize during decomposition but remains in the solid state, decomposition is not influenced by vaporization, so that a genuine pressure-time curve of thermal explosion is generated.

Figs. 6 and 7 show the pressure-time curves measured for the deflagration of two examples: 1,3-diphenyltriazene and hydroxylamine sulfate. In these curves the rate of pressure rise increases over most of the curve. As a first approximation they are exponential functions of time, in other words, as a first appoximation dp/dt is proportional to p. This is the classical behaviour of deflagration as described in the literature for the burning of rocket fuels [2, 7].

This is shown better in fig. 8 where the rate of pressure rise is plotted versus pressure. The first part of the pressure-time curves transformed into this diagram generate straight lines. The substances 1,3-diphenyltriazene and hydroxylamine sulfate mentioned above have a slope of nearly 1, the same as 1-nitrosonaphthol-2 plotted in the same figure. So we see here clearly that the rate of pressure rise is approximately proportional to the pressure. This is not valid for the fourth substance in this diagram, ammonium dichromate, which has a steeper slope in this diagramm from which it can be concluded that the rate of pressure rise is approximately proportional to p^2.

Merzhanov [8] has made a theoretical study of the pressure-dependence of the deflagration rate. The proportionality of dp/dt to p is readily understandable if the flame zone of deflagration is in the gas phase. According to the theory of flame propagation in the gas phase the rate of flame propagation is independent of pressure if only second order reactions occur. However, the flow rate through the flame zone is then proportional to the density and hence proportional to pressure. These considerations cannot be applied to ammonium dichromate because it surely has no gas phase reaction zone.

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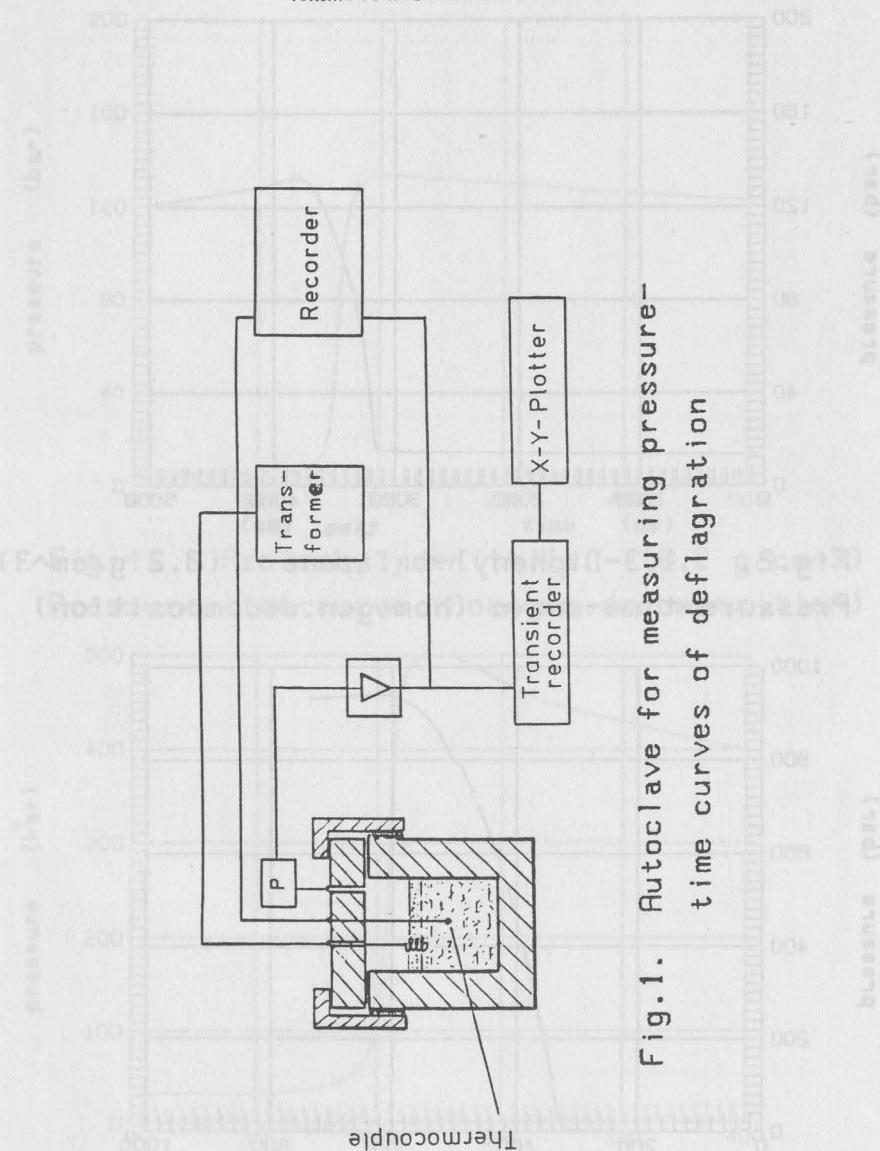
Fig.1. Autoclave for measuring pressure-time curves of deflagration
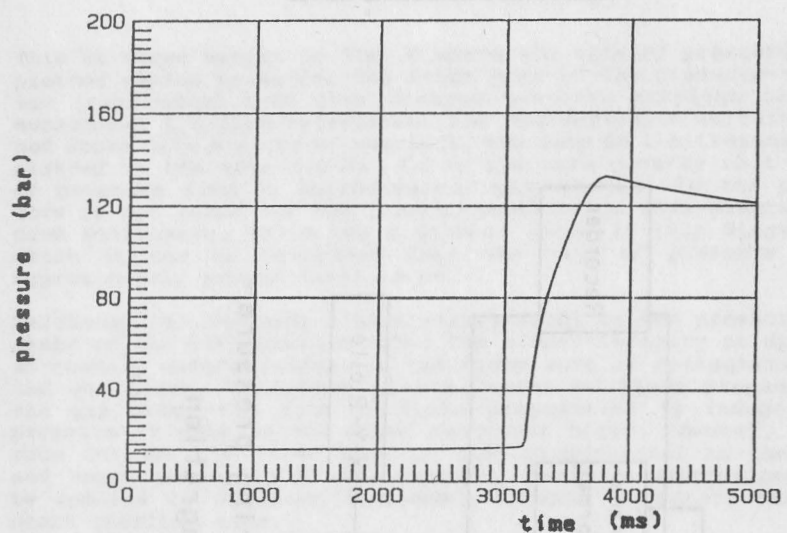
Fig.2.   1.3-Diphenyl-triazene   (0.2 g/cm^3)
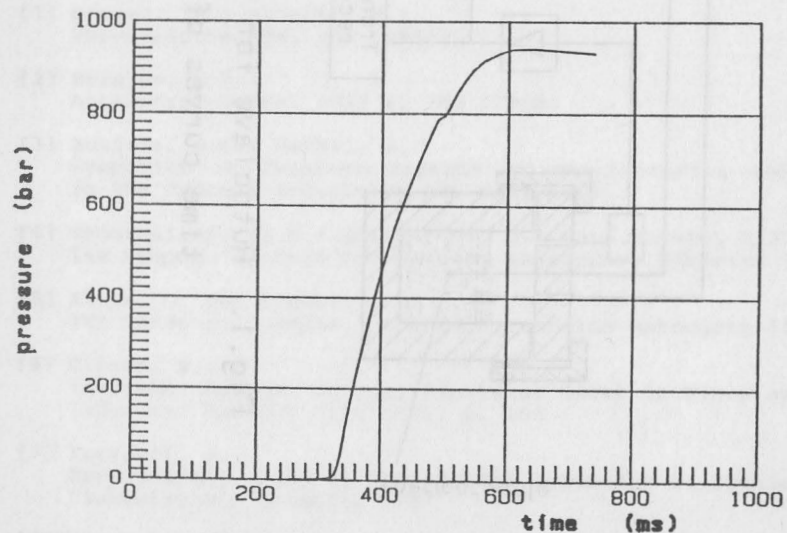Pressure-time-curve (homogen.decomposition)

Fig.3.   2-Nitrobenzaldehyde   (0.2 g/cm^3)
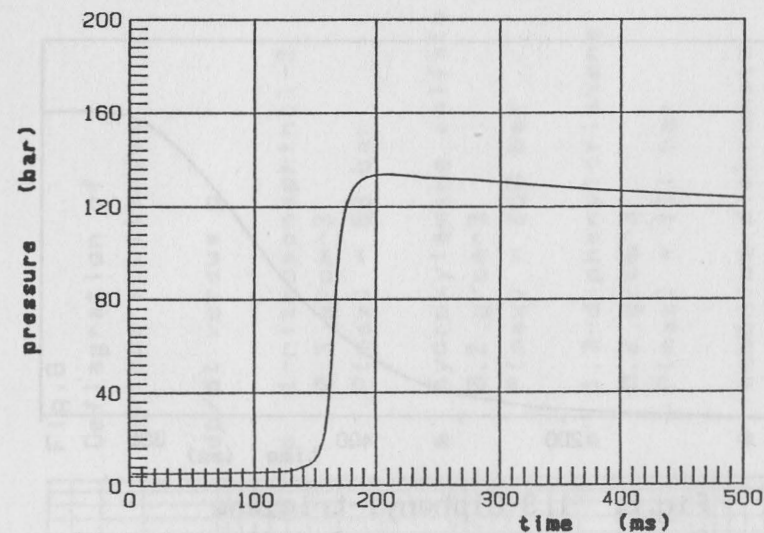Pressure-time-curve (homogen.decomposition)

Fig.4.   Azoisobutyronitrile   (0.2 g/cm^3)
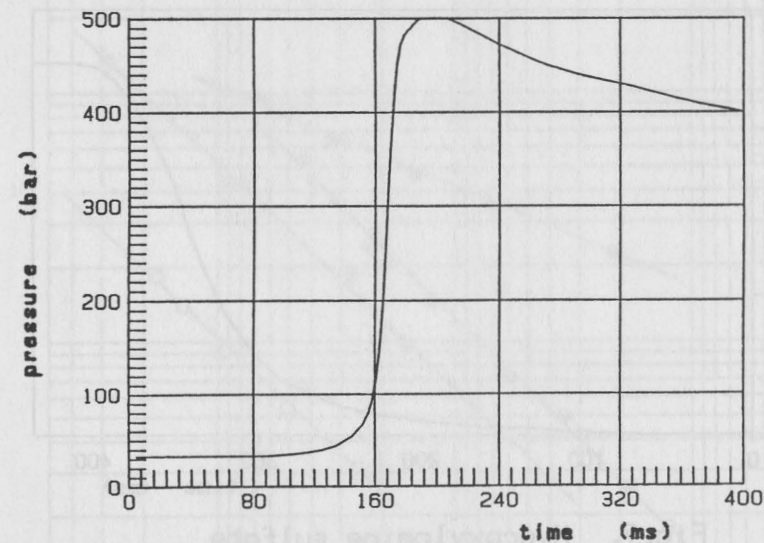Pressure-time-curve (homogen.decomposition)

Fig.5.   Ammonium dichromate   (0.2 g/cm^3)
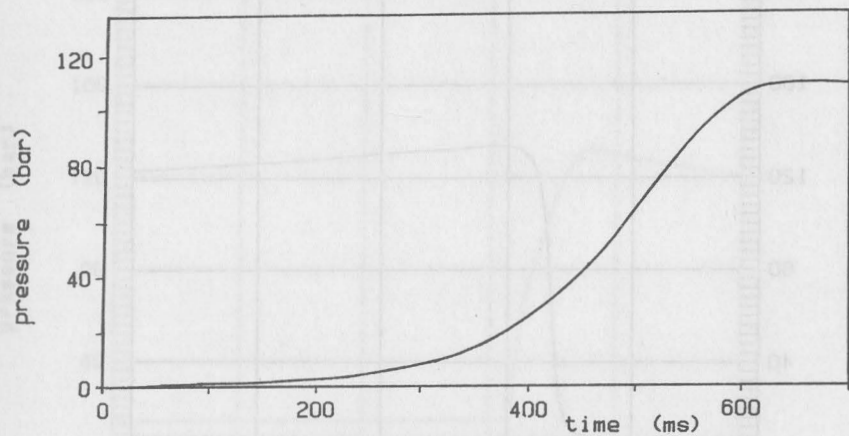Pressure-time-curve (homogen.decomposition)

Fig. 6.   1.3-Diphenyl-triazene
Pressure-time-curve of deflagration
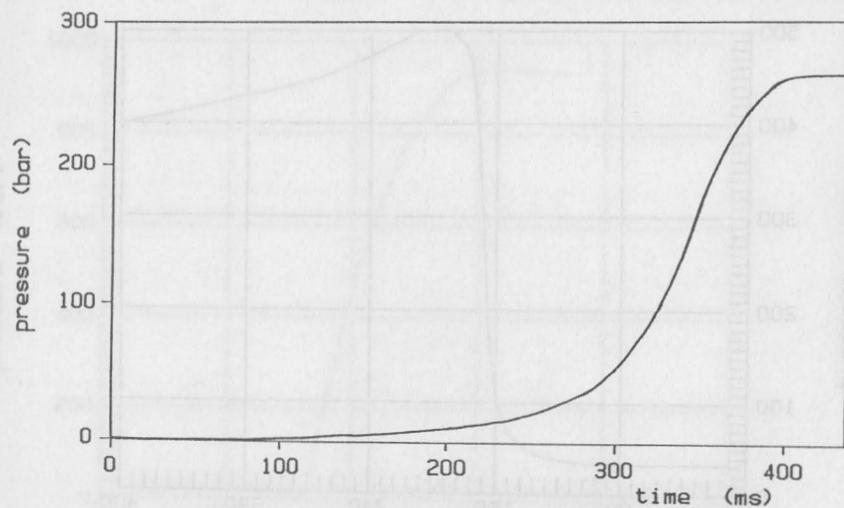0.2 g/cm^3 , 200 cm^3 autoclave

Fig. 7.   Hydroxylamine sulfate
Pressure-time-curve of deflagration
0.2 g/cm^3 , 200 cm^3 autoclave

Fig.8
Deflagration of
various substances

dp/dt versus p

o 1-nitrosonaphthol-2
   0.3 g/cm^3
   P(max) = 68 bar

⊕ hydroxylamine sulfate
   0.2 g/cm^3
   P(max) = 250 bar

⊖ 1.3-diphenyltriazene
   0.2 g/cm^3
   P(max) = 111 bar

● ammonium dichromate
   0.2 g/cm^3
   P(max) = 252 bar