DETERMINATION OF THE EFFECT OF A THERMAL EXPLOSION OF ORGANIC PEROXIDES (HOMOGENEOUS EXPLOSION TEST)

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Summary

In this paper an instrument for investigating the pressure effects caused by thermal explosions of such unstable substances as organic peroxides is described.

The design of the instrument makes it possible to simulate situations with a moderate degree of confinement. A number of intermediate scale experiments have been carried out to investigate the applicability of the results of this laboratory instrument for practical purposes. Within the limits of experimental accuracy a good agreement between laboratory and intermediate scale results is obtained. In the employed configurations with moderate confinement the thermal explosion of peroxides is found to give relatively weak pressure effects, the magnitude of which strongly varies in accordance with chemical constitution.

Introduction

The phenomenon of thermal explosion is well known (see for instance [1—3]). In general every exothermal reaction may, depending on the external conditions, lead to a thermal explosion. A good understanding of the thermal explosion is important for the safe handling, storage, production and transportation of many industrial chemicals such as organic peroxides [4]. The initial thermal conditions leading to an explosion are well understood and in principle it is possible to calculate parameters such as critical temperature, critical dimensions and the induction period in which an explosion can be expected. For the determination of the necessary self-heating parameters several test methods are available, for instance the adiabatic storage test [5], isothermal storage test [6] and various practical self-heating tests such as Wärmestau Verfahren [7] and the SADT test [8,9].

More complicated is the description of the thermal explosion itself and the physical events, like pressure and temperature effects, accompanying the explosion. In the past many tests have been developed to assess the behaviour of unstable substances when involved in a fire. The Dutch pressure vessel test [10] and the German steel tube test (Stahlhülsen Verfahren) [11], which are described in RID [12], are well-known. The results of these tests can only

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be used in a comparative way since both techniques do not give values which can be extrapolated to practical conditions.

More quantitative data are obtained with such test methods as the time-pressure test [13] and the Janaf test [14]. These two tests are relatively simple and in concept restricted to the determination of the thermal explosion effect of a sample in a closed pressure vessel.

The present instrument enables one to measure the characteristics of the effect of a thermal explosion under external circumstances simulating conditions which are met in practice. Much attention is paid to the confinement of the substance. Furthermore the instrument is equipped with practical provisions such as a bursting disk, variable heating rates and an outer chamber which serves as an expansion chamber for the explosion products. The extent to which the results of this instrument can be extrapolated to large scale events is discussed. The investigations are restricted to the thermal explosion of solids and liquids, and secondary explosions are explicitly avoided. The latter may occur when the gaseous products of the primary thermal explosion form a combustible mixture with the ambient air.

Apparatus

The apparatus (see Fig. 1) is made of stainless steel and consists of two compartments: a sample holder (1) containing the sample; and an expansion chamber (2) in which the explosion products (foam, gases etc.) are contained. The volumes of these compartments are 10^{-4} and 10^{-2} m^3 respectively. The whole apparatus is designed for a working pressure of 3.0 MPa* and a maximum temperature of 600 K and is provided with a rupture disk (3) with a bursting pressure of 3.6 MPa.

To prevent evaporation of the sample and to give the sample a moderate confinement the holder is closed at the top with a teflon-coated aluminium membrane (4). The bursting pressure of this membrane can be varied to simulate different degrees of confinement. A small (capillary) tube (5) connects the sample holder with the expansion chamber. This connection serves as a venting valve to equalize the pressure between the two compartments in the early stages of decomposition. The capillary tube is made of teflon and has an internal diameter of 1.6×10^{-3} m and a length of 2 m so that evaporation is minimal.

The apparatus is provided with an external primary heating coil (7) and an additional secondary heating coil (8) around the sample holder. The primary coil is wound in such a way that a uniform temperature distribution along the whole apparatus is achieved. The temperature of the apparatus is regulated by a programmable temperature control unit. (Haake, type TP 32). The heating rate $\dot{T}$ is a linear function of time and is variable between 0.56 mK/s and 50 mK/s (2 to 180° C/h). The purpose of the secondary heating coil is to

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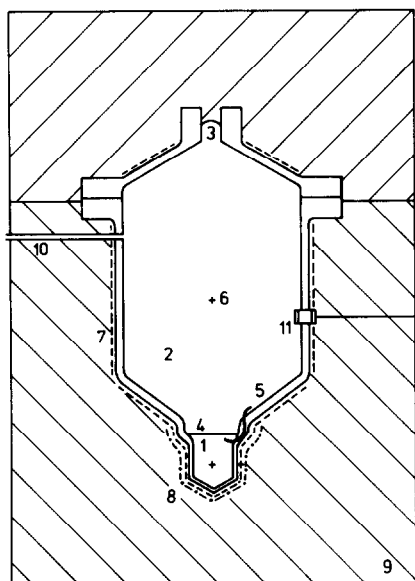*1 MPa $= 10^6$ N/m^2 = 10 bar.

Fig. 1. Homogeneous explosion test apparatus. 1 sample holder, 10^{-4} m³; 2 expansion chamber, 10^{-2} m³; 3 bursting disk, 3.6 MPa; 4 teflon-coated aluminium disk, 0.05—0.35 MPa; 5 capillary tube, length 2 m, diameter 1.6×10^{-3} m; 6 + symbol, used for thermocouple; 7 primary heating coil ------; 8 secondary heating coil — · — · — ·; 9 insulation; 10 pressure gauge connection; 11 pressure transducer.

compensate for heat losses from the sample when self-heating is encountered. The power supply of the secondary heating automatically keeps the small temperature difference between the centre of the sample and the wall of the sample holder constant, thus providing a quasi-adiabatic self-heating of the substance. The whole apparatus is thermally insulated.

During the test the temperature is measured inside the sample and in the centre of the expansion chamber. The absolute pressure is determined by means of a Bourdon-gauge, and the rapid pressure change during the explosion with a piezo electric pressure transducer (Kistler). All relevant signals are recorded on a four channel instrumentation tape recorder (Hewlett Packard 3960). Since the presence of oxygen from the air may lead to a secondary explosion of the reaction products, the expansion chamber is filled with nitrogen at the start of each test.

Results

The results of a typical measurement with bis(4-t-butyl cyclohexyl) peroxydicarbonate (technically pure) are given in Figs. 2 and 3.
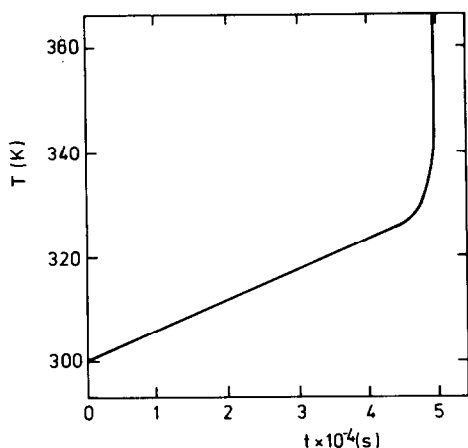
Fig. 2. Temperature vs. time curve of 50 g bis(4-t-butyl cyclohexyl) peroxydicarbonate at an external heating rate of 0.56 mK/s.
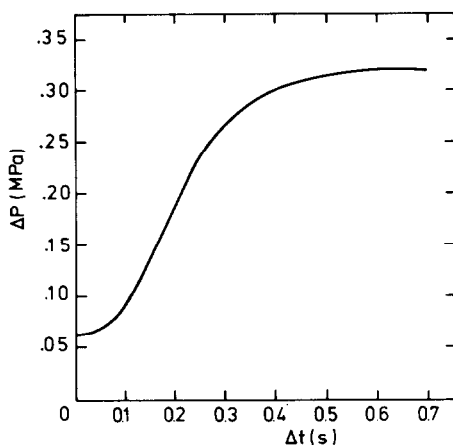
Fig. 3. Overpressure vs. time curve of 50 g bis(4-t-butyl cyclohexyl) peroxydicarbonate at an external heating rate of 0.56 mK/s. Maximum pressure rise is 1.11 MPa/s.

The temperature versus time curve in Fig. 2 shows a linear change in the sample temperature due to external heating and a subsequent asymptotic rise in temperature caused by the thermal decomposition of the sample.

For the particular heating rate of 0.56 mK/s (2°C/h) the self-heating of the substance becomes noticeable at about 328 K. The temperature at which the self-heating rate equals that of the artificial external heating, i.e. dT/dt is twice the external heating rate, will be defined as T_0. The curved line in Fig. 3 represents the pressure effect accompanying the explosion. The derivative at the inversion point yields the maximum pressure variation, $(dp/dt)_{max}$. The starting time in the plot is chosen arbitrarily and the pressure at that time is due to the expansion of the gas in the expansion chamber and the early decomposition and evaporation of the sample. The explosion parameters which can be obtained from these graphs are: the temperature T_0 = 328 K, the maximum pressure flux, $(dp/dt)_{max} = \dot{p}$ = 1.11 MPa/s, the maximum pressure, p_{max} = 0.42 MPa and finally, not shown in the graphs, the maximum temperature recorded in the expansion chamber, T_{max} = 620 K. The latter will be lower than the actual temperature occurring in the explosion products due to the relatively slow response time of the thermocouple.

The explosions are not always as simpe as in the case treated here. An illustrative example of a more complex explosion phenomenon is given in Figs. 4 and 5.

At a heating rate of 0.56 mK/s (2°C/h), t-butyl peroxy isopropylcarbonate (technically pure) is found to explode in two stages with pressure fluxes of
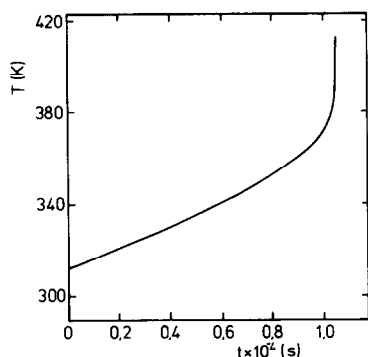
Fig. 4. Temperature vs. time curve of 100 g t-butyl peroxy isopropylcarbonate at an external heating rate of 0.56 mK/s.
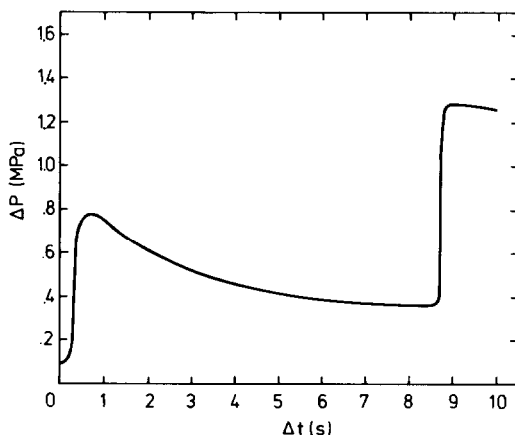
Fig. 5. Overpressure vs. time curve of 100 g t-butyl peroxy isopropylcarbonate at an external heating rate of 0.56 mK/s. Maximum pressure rises are 12 MPa/s and 7.1 MPa/s respectively.

12.0 and 7.1 MPa/s respectively. This multiple stage effect may be due to consecutive decomposition reactions of this particular peroxy compound. At higher heating rates the distinction between the two pressure slopes becomes less clear and vanishes at the highest rate that has been employed, 50 mK/s (180° C/h).

For a number of peroxides the pressure effects have been investigated more systematically. The results are given in Table 1. All substances listed in the table are of technical quality (supplier: Akzo Chemie B.V.)

To obtain uniformity in the representation of the pressure parameters the following reduced quantities are introduced[*].

$$P_s = p_{max} \ V/m \quad \text{and} \quad \dot{P}_s = (dp/dt)_{max} \ V/m \tag{1}$$

where V is the volume of the expansion chamber and m the mass of the sample. The reduced parameters are used for scaling up the experimental values p_m and $\dot{p}_m$ when dynamic effects are absent. The experiments are carried out at a bursting pressure of 0.07 MPa for the aluminium membrane and a heating rate of 0.56 mK/s (2° C/h). In the case of multiple stage effects only the highest $\dot{P}_s$ value is tabulated. Table 1 shows that distinctive differences in pressure fluxes do occur. The values vary from 0.4 kGy/s for cumyl hydroperoxide 80% to 1.5 MGy/s for t-butyl peroxy isopropylcarbonate. The three substances at the bottom of the list show very weak effects, which can be at-

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[*]Similar quantities are used for gas and dust explosions. A direct comparison with this type of explosion is not possible as different scaling parameters apply.

tributed to a sufficiently high dilution with an appropriate solute. The differences in maximum pressures are much less, as they all lie in the range of 5 to 115 kGy. The values given in Table 1 are specific for the given heating rate and bursting pressure. Both quantities P_s and in particular $\dot{P}_s$ vary with these external parameters.

TABLE 1

Explosion effect parameters P_s and $\dot{P}_s$ at 0.56 mK/s heating rate and 0.7 MPa membrane bursting pressure

Chemical compound	P_s (kGy)**	$\dot{P}_s$ (kGy/s)
t-Butyl peroxy isopropylcarbonate	115	1500
t-Butyl peroxybenzoate	75	230
Bis(4-t-butyl cyclohexyl) peroxydicarbonate	50	170
1,3-Bis(t-butyl peroxy-isopropyl) benzene 96%	75	90
Di-n-butyl peroxydicarbonate 25% in isododecane	5	0.5
Cumyl hydroperoxide 80%	21	0.4
t-Butyl hydroperoxide 70% in water	Evaporation only*	

*If the pressure in the expansion vessel before the test is elevated to 0.5 MPa (to prevent evaporation), these parameters are P_s = 64 kGy and $\dot{P}_s$ = 0.3 kGy/s.
**1 Gy = 1 Pa m³ kg.

Influence of experimental parameters on the results of the test

The reliability of the data has been checked. For a number of substances the experiments were repeated under exactly the same conditions. In general the results were found to be reproducible within 20%. Furthermore the instrument was modified to study the influence of both the sample mass and the size of the expansion chamber on the course of the explosion. Two different sample holders with a volume of 10^{-4} and 2.5×10^{-4} m³ respectively in combination with a 2×10^{-2} m³ expansion chamber were used. These tests indicated that the pressure effect parameters p_{max} and $(dp/dt)_{max}$ change linearly with the mass of the sample. By changing the volume of the expansion chamber from 2×10^{-2} to 10^{-2} m³ for a sample holder of 10^{-4} m³, both maximum pressure and pressure flux are found to increase by a factor of 2. Combining the results and using the reduced parameters defined in eqn. 1, experiments suggest that P_s and $\dot{P}_s$ are constant for each peroxide provided that the confinement is moderate and the volume of the expansion chamber is large compared with the sample size.

With the aid of these phenomenological relations the results of the inter-

mediate scale tests are also found to be mutually consistent. Hence the reduced quantities P_s and $\dot{P}_s$ are used for a mutual comparison of the results from different geometries.

The special design of the instrument makes it possible to study the effect of the thermal explosion when different heating rates are applied to the sample. The external heating of the sample holder can be varied from almost zero, simulating an adiabatic self-heating, to a rate as high as 50 mK/s (180° C/h). The influence of the heating rate on the explosion parameters of a sample of t-butyl peroxy isopropylcarbonate is shown in Figs. 6 and 7. The maximum pressure increases with the heating rate and an even stronger increase is observed for the pressure flux.

The accuracy of the measurements is found to decrease at higher heating rates. While at lower rates an almost homogeneous thermal explosion is
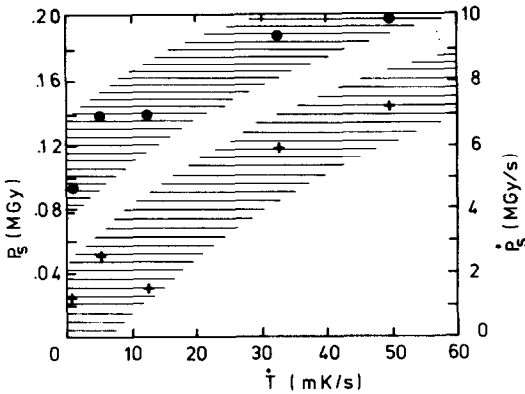
Fig. 6. Maximum reduced pressure P_s (•) and maximum reduced pressure flux $\dot{P}_s$ (+) as a function of the heating rate $\dot{T}$ for t-butyl peroxy isopropylcarbonate. Bursting pressure of the membrane is 0.07 MPa.
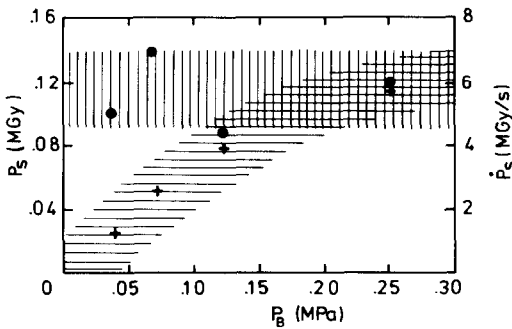
Fig. 7. Maximum reduced pressure P_s (•) and maximum reduced pressure flux $\dot{P}_s$ (+) as a function of the bursting pressure P_B for t-butyl peroxy isopropylcarbonate. The programmed heating rate is 5.0 mK/s.

achieved in the instrument, nonuniformities in the sample temperature do occur at the higher rates. In particular for solids, heterogeneous thermal explosions are all but unavoidable. This phenomenon influences the reproducibility of the measurements.

A series of experiments were carried out for different bursting strengths of the membrane. The bursting pressure was varied from 0.04 to 0.25 MPa which covers the usual degree of confinement. The results for t-butyl peroxy isopropylcarbonate, given in Figs. 6 and 7, show a maximum pressure which is almost independent of bursting strength and a pressure flux which increases with the bursting pressure. The effect at the highest bursting strength is sometimes less accurate as incomplete bursting of the foil slows the pressure build up in the expansion chamber.

For the two external parameters bursting strength and heating rate, the influence on p_{max} is generally moderate, while $\dot{p}_{max}$ is much more sensitive but does not change more than one order of magnitude. However, complementary experimental data are needed to arrive at definite conclusions.

Experimental set-up of the intermediate scale experiments

The intermediate scale experiments were performed to compare the effect of a thermal explosion at this scale with the results of the laboratory instrument. The tests were carried out with 4—100 kg of peroxide in an electrically heated sample holder (see Fig. 8) placed in a bunker of 23 m^3.

The cylindrical steel sample holder had a height/diameter ratio of 5:2 and was provided with an internal heating coil, an external heating coil, a bursting disk of 0.1 MPa overpressure, a relief vent (a tube: length 2 m, diameter 1.5×10^{-3} m) and a spray ring through which nitrogen was introduced into the sample to obtain mixing and thus a homogeneous temperature distribution. The bunker was filled with nitrogen to prevent a secondary explosion of the gaseous reaction products.

Results and discussion of intermediate scale experiments

The results of the intermediate scale experiments are given in Table 2. All experiments were performed with a heating rate of 5 mK/s (18° C/h). The reduced quantities P_s and $\dot{P}_s$ in the last two columns of Table 2 are obtained from p and $\dot{p}$ by using eqn. 1 where the expansion space parameter V now represents the volume of the bunker and m the mass of the sample.

For each peroxide the reduced parameters P_s and $\dot{P}_s$ are indeed found to be independent of the amount of peroxide used in the experiment. An arrangement of the measured peroxides according to their $\dot{P}_s$ values agrees with a similar hazard classification as found with the laboratory instrument.

The smallest effect is observed for t-butyl hydroperoxide 70% in water. The laboratory experiments show that this effect is mainly due to evaporation. The greatest effect is measured in t-butyl peroxybenzoate, where a remarkably
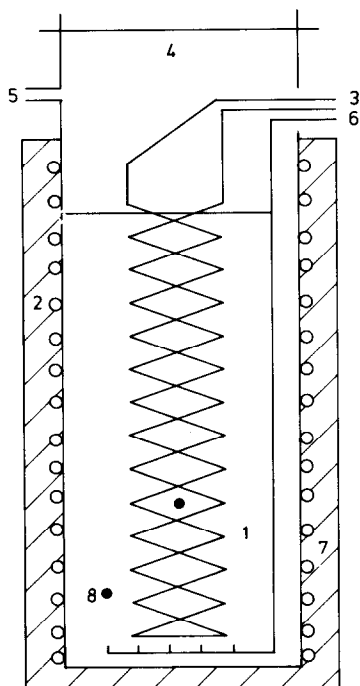
Fig. 8. Sample holder for the intermediate scale tests. 1 peroxide; 2 external electric
heating; 3 internal heating coil; 4 bursting disk, 0.1 MPa; 5 tube connector; 6 spray
ring; 7 insulation, glass wool; 8 thermocouples (•).

great effect is measured with a vessel containing 100 kg of the substance. This
exception may be due to an unknown factor in the confinement (e.g. ex-
ceeding a critical liquid height). The conditions for which such extraordinary
effects can be expected are under investigation at present.

   In Table 3 a comparison is made between the effects measured with the
laboratory instrument and those of the intermediate scale experiments. The
peroxides are arranged according to their $\dot{P}_s$ effects. Taking into account the
scaling factor in the amount of peroxide, i.e. a factor 250, and that of the ex-
pansion volume, i.e. a factor 10^3, the deviations in the results of both types of
experiments are not significant. Consequently the results of the laboratory
instrument are not only indicative of the effect of the thermal explosion but
are also suitable for extrapolation to quantities of practical importance.

Conclusions

   A laboratory instrument, equipped with separated sample holder and ex-
pansion chamber, for studying thermal explosion effects which might happen
in normal practice, is found to work satisfactorily. The effects measured in

TABLE 2

Survey of the results of the intermediate scale experiments in a bunker with a volume of 23 m^3.

Compound	Sample holder		Sample mass (kg)	$\bar{p}_m$ (kPa)	$\dot{p}_m$ (kPa/s)	P_s (kGy)	$\dot{P}_s$ (kGy/s)
	Diameter (m)	Height (m)					
t-Butyl peroxybenzoate	0.15	0.36	4	30	28	172	161
	0.21	0.48	10	50	65	115	150
	0.26	0.69	25	80	160	74	148
	0.40	1.16	100	480	60,000*	110	13800*
1,3-Bis(4-t-butyl peroxy-isopropyl) benzene, 96%	0.15	0.36	3.1	10	6	74	44
	0.20	0.47	8.1	28	17	80	48
	0.26	0.69	18.2	50	30	63	38
	0.40	1.16	80	215	95	62	27
Cumyl hydroperoxide, 80%	0.26	0.69	25	120	14	112	13
	0.26	0.69	25	105	9	97	8
t-Butyl hydroperoxide 70% in H$_2$O	0.26	0.69	25	Evaporation only			
65% in H$_2$O	0.26	0.69	25	Evaporation only			

*Sample holder fragmented.

TABLE 3

Comparison between laboratory and intermediate scale tests

Compound	Laboratory test		Intermediate scale test	
	P_s (kGy)	$\dot{P}_s$ (kGy/s)	P_s (kGy)	$\dot{P}_s$ (kGy/s)
t-Butyl peroxybenzoate	75	230	120	150[*]
1,3-Bis(t-butyl peroxy-isopropyl)benzene, 96%	74	90	70	40
Cumyl hydroperoxide, 80% pure	21	0.4	110	10
t-Butyl hydroperoxide, 70% in water	Evaporation only			

[*]The results for the 100 kg sample have been disregarded.

the instrument are shown to reproduce the effect of intermediate scale experiments with quantities of 4 to 100 kg of organic peroxides in bunkers with a volume of 23 m^3. For the cases of slight and moderate confinements of peroxide samples investigated, relatively weak explosion effects were observed. Reduced pressure parameters of a simple form were established which enable the mutual comparison of explosion effects in different geometries provided that the volume of the expansion chamber is large as compared with the volume of the sample.

Alteration of the bursting disk strength and/or the applied heating rate results in a sizeable variation of the pressure flux and a small change in maximum pressure. No systematic relations can be given as only two peroxides have been fully investigated.

The tests were performed in an inert nitrogen atmosphere to prevent secondary explosions of the gaseous reaction products. Since the temperatures measured in the vapour cloud are already as high as 300 to 500° C, selfignition of the vapour cloud is most likely to occur in the presence of oxygen.

The experiments performed so far are restricted to moderate confinements. Preliminary experiments with stronger confinements of the sample had shown that the effect of explosions increases.

Acknowledgements

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