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MEASUREMENTS OF EXPLOSION PRESSURES IN CALORIMETRIC BOMBS

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ABSTRACT

In this paper the effects of explosion pressure measurements on solids (benzoic acid and picric acid) as well as on different liquids (hexamethyl-disiloxane, benzene, tetramethyl-silane, tetramethyl-dihydrogen-disiloxane and pentamethyl-monohydrogen-disiloxane) in the presence of compressed oxygen ($p(O_2) \leq 40$ bar) within a calorimetric bomb are described. The test results permit a systematic representation of the combustion behaviour under the conditions mentioned.

INTRODUCTION

In this paper the results of explosion pressure measurements tested on different solid and liquid substances using a calorimetric bomb as reaction vessel are presented. The investigations of the combustion behaviour of solids and liquids were initially stimulated by an accident that happened in the research laboratory of a German chemical company (ref. 1).

The results of the investigations render possible the systematic classification of the combustion behaviour of the mentioned classes of substances under conditions prevailing in calorimetric bombs. This report is also aimed at contributing to increasing safety in connection with combustion-calorimetric investigations.

EXPERIMENTAL DETAILS

Explosion pressure measurements

The tests were carried out with a commercially obtainable calorimetric bomb, with an additional hole in the lid.

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A high pressure quartz transducer (type 6221A produced by Kistler Instrumente AG) was placed in this hole. The membrane of the pressure transducer was thermally protected with a paste (Oxigenoex F 25 produced by Klüber Lubrication KG, thickness of layer 1mm). The combustion of the liquids as well as the solids took place in a quartz-glass crucible inside the calorimetric bomb. Ignition was effected by means of a cotton wool thread, serving as a wick during the combustion of liquids. The wick itself was ignited as usual with an incandescent wire.

Investigation of the combustion behaviour with a high-speed camera

During these investigations a window bomb (diameter of the window 62 mm, thickness 15 mm, inside width of the window 40 mm) was used. The combustion of liquids was effected as described above. With these test series the volume of the liquid used was alsways 1.00 ml and the oxygen pressure 30 bar. The combustion pressure within the window bomb was recorded using a HYCAM-highspeed camera (model 410004).

COMBUSTION BEHAVIOUR OF SOLIDS

The solids not belonging to the explosive substances (e. g. benzoic acid) burn relatively slowly even in the presence of compressed oxygen. As a consequence, both the rate of pressure rise - an expression for the intensity of the reaction - as well as the maximum pressure during the combustion process are relatively small and largely independent of the quantity of the solid substance employed.

Figure 1 illustrates the process mentioned above. It shows the time-pressure diagram during the combustion of benzoic acid within a calorimetric bomb. At this test the oxygen pressure was 40 bar, the mass of the benzoic acid used 2.0 g. As can be seen from the illustration the pressure increases slowly with a rate of about 17 bar/s and after approximately 2.3 s reaches its maximum value of 64 bar. The pressure curves - obtained during the combustion of different quantities of benzoic acid - were similar to the one presented here. Table 1 shows that the maximum pressure occurring during combustion is practically independent of the quantity of benzoic acid employed. The same applies to the rate of pressure rise.

TABLE 1

Heterogeneous combustion of solids at p (O_2) = 40 bar ($p(O_2)$ = pressure of oxygen, m = mass of the solid, p_{max} = maximum pressure, $(dp/dt)_{max}$ = maximum rate of pressure rise)

Substance	m/g	p_{max}/bar	$(dp/dt)_{max}$/bar s^{-1}
Benzoic acid	0.5	59	20
	1.0	59	14
	2.0	64	17
Picric acid	0.5	98	3 600
	1.0	150	14 000
	1.5	216	54 000

This experimental result can be explained as follows: the benzoic acid in the quartz-glass crucible burns only at the surface. The speed of the process is limited by relatively slow transport processes - e. g. the diffusion of the oxygen to the surface of the solid substance, transport removal of the reaction product as well as heat conduction processes. Caused by the slow combustion reaction, sufficient heat can be released and absorbed by the calorimeter or by the environment. This indicates that it is mainly the gas within the calorimeter which serves to transport the heat emitted during the reaction process.

Under conditions usually prevailing in a calorimetric bomb explosive substances (ref.2) can be made to deflagrate or even detonate. In such a case very high explosion pressures as well as very high rates of pressure rise can be observed, which futhermore depend largely on the quantity of the substance employed.

The data of picric acid are presented here as an example of an explosive substance. Both the maximum explosion pressure as well as the rate of pressure rise depend, in this case - as can be seen from table 1 - largely on the quantity of the picric acid employed. The high values of the rate of pressure rise also deserve special attention.

In this case it is important for the safety during work with the calorimetric bomb to consider the large dependency of the maximum explosion pressure on the quantity of picric acid used. The reason for this is the high value of the rate of pressure rise and - connected to this - the high value of the reaction rate, which can likewise be observed with small quantities of picric acid - as can be seen from table 1. This is the reason for the combustion reaction to show an approximately adiabatic behaviour. The combustion energy serves practically only to heat the gaseous reaction products and the surplus of oxygen. It causes - besides the production of gaseous reaction products - the high and quantity-dependent explosion pressures.

COMBUSTION BEHAVIOUR OF LIQUIDS

According to the results obtained from liquids it is possible to distinguish between three different cases. This statement can only be applied to non-explosive substances:

The composition of the gas phase lies outside the explosive range (ref. 3, ref. 4)(for example: benzene and hexamethyl-disiloxane at sufficiently high oxygen pressures). In this case the rate determining partial step of the combustion process is not the actual oxydation reaction; rather the overall reaction rate is determined both by the diffusion processes as well as by the time required for the heat transport from the flame to to the surface of the liquid or to the surface of the wick moistened by the liquid. As transport processes proceed comparatively slowly, the total rate of transformation is also low. The pressures occurring in the calorimetric bomb are relatively low and largely independent of the quantity of the liquid employed.

The combustion behaviour of both model substances hexamethyl-disiloxane and benzene is summarized in table 2. The results were obtained at an oxygen pressure of 40 bar. As can be seen from table 2 both for hexamethyl-disiloxane as well as for benzene pressures and rates of pressure rise are obtained, which are largely independent of the quantity of liquid used. As already mentioned above, this kind of behaviour is typical for the combustion of liquids on wicks or at free surfaces if the surrounding gas phase is not an ignitible mixture (ref. 5).

TABLE 2
Heterogeneous combustion of liquids at $p(O_2) = 40$ bar
(V = volume of the liquid, further explanations of the symbols see table 1)

Substance	V/ml	p_{max}/bar	$(dp/dt)_{max}$/bar s^{-1}
Hexamethyl-disiloxane	1.0	67	63
	2.0	59	58
	3.0	63	70
Benzene	1.0	84	36
	2.0	76	32

In the second case the composition of the gas phase lies within the explosive range. This type of behaviour can be observed with highly volatile liquids. In this case both the explosion pressure as well as the rate of pressure rise strongly depend on the mass of the liquid and on the oxygen pressure. However, this applies to molecular homogeneous substances only as long as the whole quantity used vaporizes. At a given liquid volume the rate of pressure rise grows initially with increasing oxygen pressure, passes through a maximum and reaches the value zero at high oxygen pressures.

Tetramethyl-silane serves as a model substance for those cases where the composition of the gas phase is within the explosive range. The measurements of the explosion pressure were taken at room temperature in a calorimetric bomb serving as reaction vessel. The volume of the liquid tetramethyl-silane employed was alsways 0.70 ml. The time intervals between filling the crucible and ignition were alsways 10 min. The results of these tests are summarized in table 3. As can be seen from table 3, the maximum explosion pressure rises with increasing oxygen partial pressure. In contrast, the rate of pressure rise declines with increasing values of $p(O_2)$ and reaches the value zero at 30 bar, i. e. there is no futher reaction. For the interpretation of the results of the measurements it is worth mentioning that - under the experimental conditions described above - the whole amount of liquid was already completely vapourized after 8 min at an oxygen pressure of 20 bar; i. e. the combustion reaction of the tetramethyl-silane apparently took place solely in the gas phase. As can be expected from a homogeneous combustion reaction in the gas phase - proceeding from stoichiometrical conditions - it can also be observed in this case that with increasing oxygen partial pressure the value of the maximum rate of pressure rise decreases (ref. 6). Furthermore, the unusually high value of the maximum rate of pressure rise at $p(O_2)$ = 10 bar and $p(O_2)$ = 15 bar observed is rather remarkable. In this pressure range the combustion reaction clearly proceeds as a detonation.

TABLE 3
Combustion of tetramethyl-silane
(explanations of the symbols see table 1)

$p(O_2)$/bar	p_{max}/bar	$(dp/dt)_{max}$/bar s^{-1}
10	113	265 000
15	145	60 000
20	162	4 400
30	no reaction	

The third case, in which the composition of the gas phase is out of the explosive range (as in the case considered above), has so far only been observed in the combustion of tetramethyl-dihydrogen-disiloxane as well as pentamethyl-monohydrogen-disiloxane. The compound tetramethyl-dihydrogen-disiloxane is abbreviated in the following context with TMDS and pentamethyl-monohydrogen-disiloxane with PMDS.

Table 4 shows the results of explosion pressure measurements of TMDS in a calorimetric bomb. The tests have been executed at oxygen pressures from 10 bar to 40 bar under the experimental conditions already described above.

The abrupt changes of the reaction behaviour occuring at the increase of the oxygen pressure from 15 bar to 20 bar in heterogeneous combustion reaction of the TMDS are remarkable. This becomes most evident by comparing the curves illustrated in figure 2, showing the time-explosion pressure diagram at the oxygen pressures mentioned. The value of the maximum rate of pressure rise increases in this case from 1000 bar/s to 21000 bar/s. This alteration in the reaction behaviour is also indicated by a sharp bang (in the closed vessel!) occuring at $p(O_2)$ = 20 bar. After the calorimetric bomb was opened, it could futhermore be observed that the quartz glass crucible, serving as receptacle for the liquid TMDS, had been destroyed into tiny fragments.

TABLE 4
Hererogeneous combustion of liquid tetramethyl-dihydrogen-disiloxane
(explanations of the symbols see table 1)

$p(O_2)$/bar	p_{max}/bar	$(dp/dt)_{max}$/bar s^{-1}
10	60	1300
15	75	1000
20	121	21000
25	140	40000
30	160	90000
35	158	30000
40	170	24000

The sudden change of the reaction behaviour registered at $p(O_2)$ = 20 bar as well as the unusually high maximum rate of pressure rise give rise to the suspicion that the heterogeneous combustion reaction of TMDS at high oxygen pressures - even in a relatively small volume (V = 0.3 l) - is a detonation.

Of special interest was the clarification of the question whether other siloxanes with particularly reactive H-Si-bonds also show a combustion behaviour in compressed oxygen similar to that of TMDS. Therefore the heterogeneous combustion reaction of PMDS was tested in a calorimetric bomb. During all tests the liquid was once again ignited in a quartz-glass crucible using a wick and the time-pressure diagram was measured by means of a high pressure quartz transducer.

As in the case of the analogic measurements with TMDS an abrupt change in the reaction behaviour can be observed when the oxygen pressure is increased from 25 bar to 30 bar. Once again this becomes most evident if the curves illustrated in figure 3 are compared. They show the time-explosion pressure diagram measured in the calorimetric bomb at oxygen pressures from 25 bar to 30 bar. The value of the maximum rate of pressure rise increases in this case from 60 bar s^{-1} to 38000 bar s^{-1}.

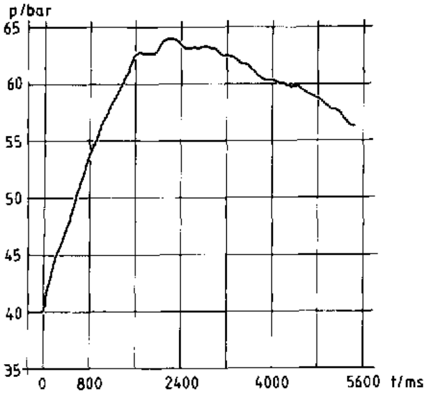

Fig. 1. Time-pressure diagram of benzoic acid combustion at $p(O_2)$ = 40 bar ($p(O_2)$ = pressure of oxygen, t = time)

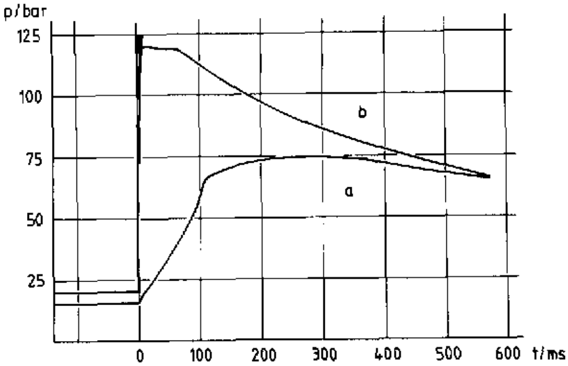

Fig. 2. Time-explosion pressure diagram of heterogeneous tetramethyl-monohydrogendisiloxane combustion at $p(O_2)$ = 15 bar (a) and $p(O_2)$ = 20 bar (b)

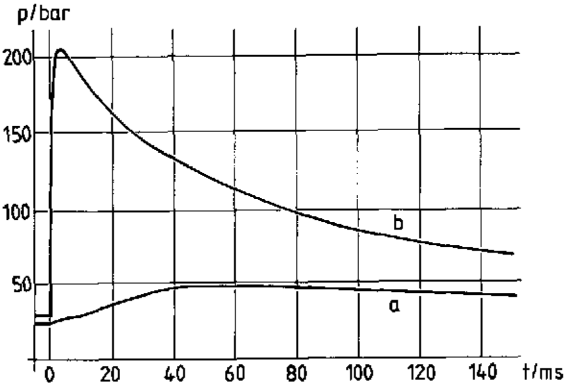

Fig. 3. Time explosion pressure diagram of heterogeneous pentamethyl-monhydrogendisiloxane combustion at $p(O_2)$ = 25 bar (a) and $p(O_2)$ = 30 bar (b)

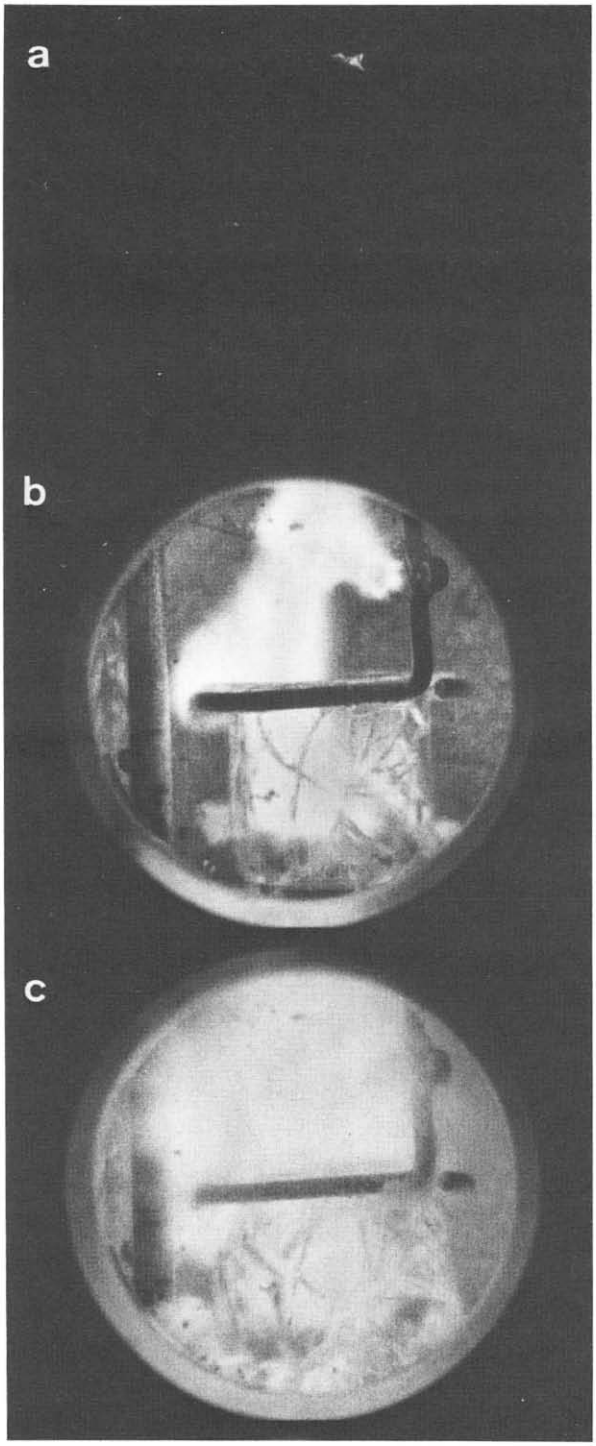

Fig. 4. Investigation of the combustion behavior of tetramethyldihydrogen-disiloxane with a high-speed camera

a) igniton of the cotton wool thread moistened with TMDS

b) 0.14 ms after ignition

c) 0.28 ms after ignition

The combustion behaviour of TMDS was also investigated using a high-speed camera. Figure 4 shows the chronological sequence of the combustion process. The photographs presented there were exposed at invervals of 1/7000 s (= 0.14 ms).

The first frame (figure 4a) shows the ignition of the cotton wool thread, moistened with TMDS, by the incandescent wire. After a mere 0.14 ms the wick is only identifiable as a flame front (see figure 4b). The reaction is so violent that the quartz-glass crucible shatters and the liquid TMDS, still on the bottom of the crucible, is dispersed. This behaviour can be explained under the assumption that the reaction of the moistened wick with the oxygen proceeds as a heterogeneous detonation. This process is responsible for the fact that the liquid TMDS, still on the bottom of the crucible, is dispersed and reacts by exploding with the oxygen in the gas room. This combustion process caused the accident mentioned.

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