



Similarities and Differences in Explosion Hazards of Organic Peroxides and High Explosives: an Experimental Study

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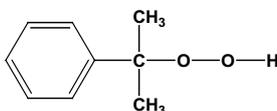
Abstract: Properties that cause explosion hazard of organic peroxides, hydroperoxides and nitrocompounds are examined in the article. Ability to thermal explosion initiation of benzoyl peroxide and of nitrocompounds is compared. Explosion properties of peroxides are analyzed. Measurements of burning temperature by means of micro thermocouples and the comparison of their values with the calculated ones of benzoyl peroxide and hydroperoxide of isopropyl benzene lead to the conclusion that burning of them propagates in condensed phase. It is noted that heat instability of benzoyl peroxide burning, contrary to many nitrocompounds, is absent. Burning of benzoyl peroxide is stable even in vacuum. It is noted that, although benzoyl peroxide is not applied as explosive, in some cases the explosion hazard of benzoyl peroxide heating can be bigger than that of PETN. This conclusion was made on the basis of an investigation carried out by means of DSC method. The explosion process of benzoyl peroxide and hydroperoxide of isopropyl benzene propagates in a regime reminiscent of a low velocity detonation and the explosive effects are sufficient for severe destructions during accidents. This conclusion unfortunately is confirmed by bitter experience in practice. The results of the investigation of condensed products of explosion at impact of mixtures aluminum with peroxides and with nitrocompounds by means of impact-testing machine that were carried out in this work by X-ray diffraction analysis are discussed. It was shown that if the temperature of explosion of a mixture is $T_p \geq 2200-2300$ K, practically all aluminum or aluminum hydride in the mixture transformed into aluminum oxide.

Keywords: explosion hazard, benzoyl peroxide, heat instability of burning, nitrocompounds

Introduction

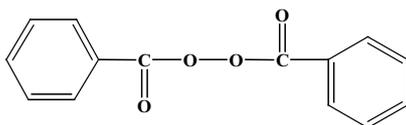
Wide application of organic peroxides and hydroperoxides [1] in chemical, polymeric, varnish-and-paint, medical branches of industry and the bare necessities of guaranteeing explosion safety arouse interest in investigation of explosion properties of peroxides and hydroperoxides [2-12]. Properties that cause explosion hazard of benzoyl peroxide (solid) and hydroperoxide of isopropyl benzene (liquid) are examined in the article because these peroxides find the widest use action.

There are some accidents during production and application of hydroperoxide of isopropyl benzene (trade name, Hyperis, CH)



that are described in literature [4-5].

There are more described accidents or unexpected explosions of benzoyl peroxide (BP)



during its application, transport and working up, although the amount of BP produced is much lower than that of Hyperis. These accidents and laboratory research data testify of a high explosion hazard of benzoyl peroxide and International Chemical Safety Cards (ICSC) characterize it as highly explosive substance, in spite of the fact that BP has never been applied as explosive. Not a long time ago (in 2003), an explosion of BP took place during drying (US Chemical and Plastics Inc.). The accident was described and investigated in work [14]. The immediate cause of explosion established at investigation of the accident was that drying of BP was carried out at a temperature that was too close to the temperature of self-ignition at heating.

Explosion hazard of a substance can be characterized by analysis of a complex of parameters: conditions of initiation of heating self-ignition (on-set temperature) and of its intensity, burning and detonation properties, sensitivity to external action, etc. Explosion properties of usual explosives (mainly nitrocompounds) are well-known and are described in detail in literature and

collections of reference data [16].

Oxygen balances and heats of explosion of peroxides and nitrocompounds under investigation that were computed according to the laws of thermodynamics by means of the Russian method SD [17] are collected in Table 1.

Table 1. Oxygen balances and heats of explosion of investigated peroxides and nitrocompounds

Substance		Q _v , MJ/kg	Oxygen balance, %
Peroxides	BP	2.34	-191.5
	HMTD ^{*)}	3.40	-92.2
	Hyperis	3.29	-231.3
	TPA ^{*)}	4.07	-151.2
Nitrocompounds	NC (12%N) ^{*)}	4.15	-38.5
	Picric acid	4.28	-45.4
	TNT	4.51	-74
	Tetryl	4.87	-47.4
	HMX	5.55	-21.6
	PETN	5.92	-10.1

^{*)} TPA is Threeperoxide of acetone, HMTD is Hexamethylenethreeperoxidediamine, and NC (12%N) is NC containing 12% N.

One can see that the oxygen balances and heats of explosion of peroxides are lower than these parameters of nitrocompounds.

Comparison of explosion properties of nitrocompounds and peroxides has not been carried out yet.

Results and Discussion

Thermal explosion of BP and Hyperis was investigated in our works [2-3] with a glass thermostat by means of the method [18].

Thermal explosion of BP was investigated at mass $m = 0.3-0.5$ g and the velocity of heating 28-23 deg/min. It was accompanied by flash and sound effect. The explosion of BP occurred in the run at sample mass $m = 0.5$ g and the velocity of heating $V = 15$ deg/min. The strength of thermal explosion in this experiment was high and destroyed the glass apparatus, even though the mass of BP was small. The results of the runs are shown in Table 2.

Table 2. Experimental results of BP behaviour at heating

Mass, g	Velocity of heating, deg/min	Beginning of decomposition		$T_{\text{flash}}, ^\circ\text{C}$	Result
		$T, ^\circ\text{C}$	t, min		
0.3	28	91	3.1	120	Flash
0.5	23	92	3.2	106	Flash
0.5	15	96	5.5	125	Explosion

Typical curves of temperature versus time at heating of both Hyperis (CH) and inert liquid (sulfuric acid for comparison) in the same conditions as BP are shown in Figure 1. The crosses in these curves mark the moment of the very beginning of the decomposition reactions of CH producing visible bubbles of gases or vapours after following approximately the linear law of CH heating. This moment coincides with acceleration of temperature increase. Gasification (pseudo-boiling) intensified at self-heating of CH, the droplets of decomposition products condensed on the wall of the test-tube and fell down. As decomposition progressed, the initially colorless substance became light brown. A flame never appeared at CH decomposition under these conditions. The induction periods and the temperatures of decomposition beginning at various velocities of heating are presented in Table 3.

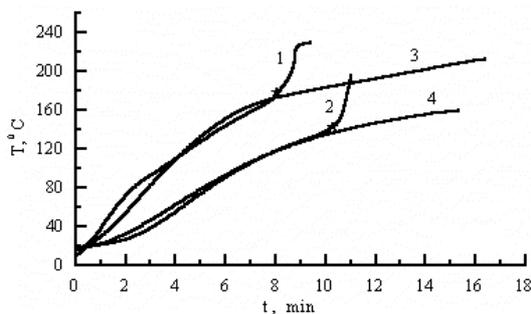


Figure 1. Experimental curves of Hyperis heating (1, 2), the crosses mark the beginning of decomposition, 3 and 4 are heating of inert substance (sulfuric acid).

Table 3. Temperature and time of the beginning of Hyperis decomposition at various velocities of heating

Velocity of heating, deg/min	Beginning of decomposition	
	Temperature, °C	Time, min
19	145	10.3
21	159	7.2
28	142	5.2
32	141	4.2
39	160	4.4
40	157	4.2
50	160	3

Experimental curves temperature (T) vs. time (t) at nitrocompounds heating at velocity of heating $\bar{u} = 23.5$ deg/min in the same glass thermostat as in the runs with Hyperis and BP are shown in Figure 2 [19]. One can see that the values of temperature and time of the beginning of decomposition of usual explosives (nitrocompounds) at heating are higher than those of benzoyl peroxide.

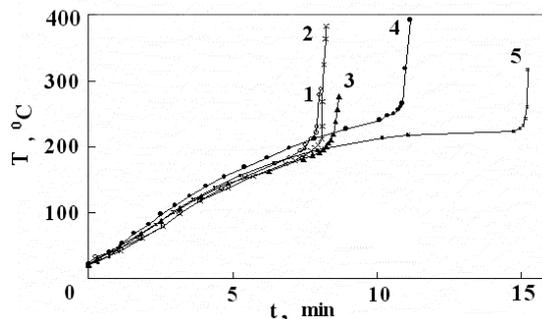


Figure 2. Experimental curves of temperature (T) vs. time (t) at nitrocompounds heating in a glass thermostat; velocity of heating is $\bar{u} = 23.5$ deg/min. 1 – Dina, 2 – Tetryl, 3 – PETN, 4 – Dinitrobenzoforoxane, 5 – RDX.

The experiments with benzoyl peroxide and with typical explosives (TNT and PETN) were carried out by Differential Scanning Calorimeter (DSC) method [18]. The method does not allow to measure the precise heat of decomposition reactions which are accompanied with gas formation and with unsteady conditions of heat loss in parallel runs, but the comparison of dependencies of heat flux vs. temperature curves of benzoyl peroxide and these of PETN and TNT, presented in Figure 3, is of interest:

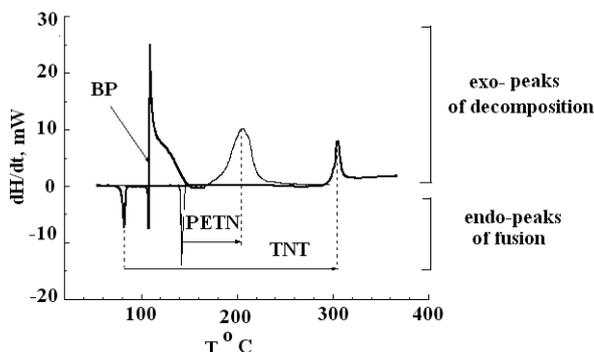


Figure 3. Comparison of DSC curves for BP, PETN and TNT.

One can see that benzoyl peroxide has lower decomposition temperature in comparison with typical explosives resulting in thermal explosion. The decomposition of BP begins immediately after its melting (i.e. at $T = 108\text{--}109^\circ\text{C}$). BP heightened sensibility to heating in comparison even with nitroester (PETN) is clear: fusion of BP at 108°C leads immediately to thermal explosion, whereas the difference between melting temperature and initial decomposition temperature of PETN is approximately $\Delta T \sim 60^\circ$. This difference is bigger in the case of TNT ($\Delta T \sim 120^\circ$) and in the case of the insensitive explosive – NTO – decomposition starts at the same temperature as its fusion [20] but it takes place at rather higher temperature $T \sim 280^\circ\text{C}$.

High explosion hazard of BP is connected with its high sensitivity to heating, in contrary to nitrocompounds, and with the high intensity of thermal explosion of BP, as it was shown in the experiments in glass thermostat.

Burning of BP had been thoroughly investigated under the direction of Professor A.E. Fogelzang at the pressure range of 0.02–40 MPa in work [10]. Not only the burning law (velocity vs. pressure) of BP was established but also temperature of burning was measured experimentally.

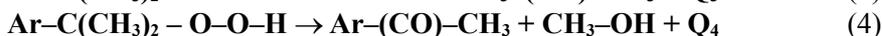
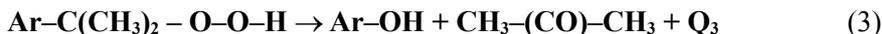
According to these measurements, the zone of maximal temperature of BP burning was found practically at the surface of burning, noticeable gasification was not present. The measured temperature of burning ($T_p = 833\text{ K}$) was much lower than the computed one according to the laws of thermodynamics. It turned out that raising temperature to the measured value ensured proceeding of exothermal reactions of decomposition of BP that was well-known from slow decomposition data:





As to the difference between the calculated and measured temperatures of burning, the same picture was observed in the case of Hyperis [2].

Reactions of slow decomposition of Hyperis that ensured rising of temperature to the measured value were:



BP burned stably at pressure that was lower than the atmospheric one. The velocity of BP burning at atmospheric pressure was higher than of usual explosives (nitrocompounds).

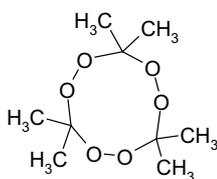
The results of investigations of BP burning indicated that reactions of its burning proceed in condensed phase. During nitrocompound burning heat storage that is needed for stable burning propagation is contained in condensed phase but the chemical reaction of burning and heat generation proceeds in the gas phase. The difference between the heat sluggishness of gas and solid is rather important. The disbalance of heat between these phases reduces the wave of burning attenuation of some nitrocompounds (e.g. TNT and PETN) at atmospheric pressure and in vacuum. The theory of heat instability of burning was described in work [21]. Heat instability is inherent to many nitrocompounds. It does not appear for BP burning because of the absence of upsetting of heat balance between gas and solid phases, and that is one more reason of high explosion hazard of BP.

According to reactions (3) and (4), acetone and methanol are formed at Hyperis decomposition, the evaporation of which probably leads to an increase in heat loss from the reaction zone, and its burning propagates at pressure $P \geq 20$ MPa. Besides, the industrial method of phenol and acetone manufacturing is based on reaction (3), and evaporation of acetone at reaction (3) proceeding is controlled from the aspect of process safety.

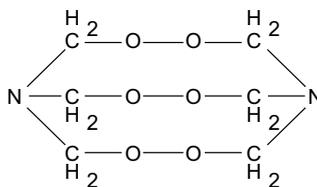
Ability of BP and Hyperis to detonate was investigated and described in works [2, 3]. Explosion process propagated in charges of BP in a crash-proof steel confinement at density $\rho = 0.4-0.6$ g/cm³ with velocity $D = 1.2-1.8$ km/s at powerful initiation (pressure of initiation $P_{in} \approx 30$ GPa, although the velocity of explosion process diminished to $D = 0.7-1.0$ km/s to the end of charge (length of the charge $L = 200$ mm, diameter $d = 10$ mm, wall thickness $\delta = 12-13$ mm). The velocity of explosion process of Hyperis in the same conditions was $D = 1.97-1.88$ km/s. The measured velocity of explosion processes of both the

peroxides was much lower than the computed detonation velocity according to the method SD [17]. The validity of that for nitrocompounds was checked out in works [22, 23]. The difference between the calculated and measured detonation velocity for these substances did not exceed 5% and sometimes it was even lower.

Ability of peroxide groups to impart explosion properties to substance can be in some cases so high that explosion hazard of them can be comparable to primary explosives. Threeperoxide of acetone (TPA) and hexamethylenethreeperoxidediamine (HMTD) can be given as examples:



TPA



HMTD

Properties of these peroxides were described in works [6-9, 11]. Detonation process occurred at usual initiation firing propagated in HMTD at density $\rho = 0.38 \text{ d/cm}^3$ with velocity $D = 2.82 \text{ km/s}$ and in TPA at $\rho = 0.47 \text{ g/cm}^3$ with velocity $D = 1.43 \text{ km/s}$. Detonation of these peroxides can initiate detonation of TNT at apparent density.

The main goal of the next step of the investigation was to detect the difference of explosion reaction proceeding in nitrocompounds and in peroxides. It has been shown in the previous investigations [13] that all aluminum turned into aluminum oxide at explosion of mixtures of it with typical energetic material such as HMX. On the contrary, aluminium oxide was not found at all after explosion of mixture of benzoyl peroxide with aluminium or with aluminium hydride at impact [24]. This fact gave an opportunity to conclude that the temperature of BP/Al explosion was not higher than fixed in work [10], i.e. it did not culminate to thermodynamic value.

In that case, the quantity of explosives – aluminum mixtures under investigation were extended. Peroxides: TATP and HMTD and nitrocompounds of various classes: C-nitrocompounds (TNT, picric acid), nitroethers (PETN, nitrocellulose (NC with a content of nitrogen, $C_N = 11.6\%$), compound that was at the same time C-nitrocompound and N-nitrocompound (tetryl) were used as the explosive base of the mixtures.

The quantity of Al (powder PAP-2) or hydride of aluminum in the mixture was equal to $C_{Al} = 10\%$. The explosion was initiated by means of impact. Tests were carried out with an impact-testing machine (Russian modification K-44-II)

in a device with hindered substance outflow. The methodology of carrying out experiments was the same as in work [13]. A sample (50 mg of mixtures) put between 2 steel rolls ($d = 10$ mm), was placed inside a steel muff. The weight (mass $m = 10$ kg) dropped down ($H = 150$ -500 mm) on upper role. The explosion products were gathered after explosion and their X-ray diffraction analysis was carried out (CuK α 1-radiation in chamber «Huber Imaging Plate Guiner Camera G670»).

Lattice constants of aluminum oxides cells that formed at explosion of some mixtures contained Al and AlH₃ are collected in works [13, 24].

The results of condensed products of explosion analysis are shown in Table 4. As one can see, formation of aluminum oxide takes place at explosion of mixtures of high explosives (tetryl, HMX, PETN) with aluminum or aluminum hydride. Aluminum oxide was not practically formed at explosion of mixtures of C-nitrocompounds (TNT and picric acid) with Al or AlH₃.

Aluminum oxide was found in the explosion products of mixture with aluminum of only one substance from the class of peroxides (HMTD); aluminum oxide was not formed practically at the explosion of mixtures on base of BP and TPA with aluminum. The data of analysis and calculated temperature of explosion (T_p) are collected in Table 4.

Table 4. Calculated explosion temperature (T_p at pressure $P = 150$ MPa) by means of the method [25, 26] taking into consideration the contents of condensed products of explosion, found experimentally

No.	Mixtures	T_p , K	Condensed products of explosion, found experimentally, mol/kg	
			Al ₂ O ₃	Al
1	BP/ Al	833 ^{*)}	-	3.70
2	TPA / Al	1977	0.003	3.70
3	TNT/ Al	2026	0.003	3.70
4	NC/ Al	2096	0.12	3.46
5	Picric acid/AlH ₃	2127	0.001	3.33
6	HMTD /Al	2201	1.61	0.48
7	NC/AlH ₃	2327	0.95	0.37
8	Tetryl/AlH ₃	3111	1.67	-
9	HMX/AlH ₃	3474	1.65 ^{**)}	-
10	PETN/AlH ₃	3781	1.67	-
11	HMX/Al	3802	1.83 ^{**)}	-
12	PETN/Al	4019	1.76	0.18

^{*)} Temperature of BP burning that was measured in work [10].

^{**)} Calculated values.

The temperatures of explosion of mixtures (T_p) were calculated by means of the method [25, 26], that presumed to take into consideration the composition of condensed products of explosion found experimentally.

The data of Table 4 demonstrate that aluminum oxide does not arise at explosion of mixtures, the T_p of which is lower than 2200 K (BP/Al, TPA/Al, TNT/Al, NC/Al). If the temperature of explosion of a mixture is $T_p \geq 2200$ -2300 K, practically all aluminum or aluminum hydride in the mixture of it with an explosive (picric acid, HMTD, NC, tetryl, PETN, HMX) transforms into aluminum oxide.

Conclusion

In terms of these results one can make conclusion that chemical reactions at explosion of mixtures of peroxides with aluminum or aluminum hydride and HMX with aluminum or aluminum hydride are quite different. The temperatures of explosive transformation of mixtures BP/Al, TPA/Al are lower than these of mixtures of Al with HMX, PETN and HMTD. This temperature is not sufficient for transformation of aluminum and aluminum hydride into aluminum oxide. It may be added that the initial products of decomposition of nitrocompounds (NO_2) are essentially different from the ones of BP (reaction 1 and 2). These products can oxidize not only C and H to CO_2 and H_2O but even aluminum to Al_2O_3 at the temperature of explosion $T_p \sim 800$ K.

However, the temperature of explosion is probably the main parameter that leads to transformation of Al in mixtures with explosives into aluminum oxide – explosive components of mixtures that generate aluminum oxide in the products of explosion (6-12 in Table 4) are substances of various classes: peroxide, C-nitrocompound, N-nitrocompound and nitroether.

It must be noted that pressure at explosion process of BP propagating with velocity $D \approx 1$ -2 km/s is approximately $P \approx 0.5$ -1 GPa, in other words, shock wave generated by such explosion process or by thermal explosion of large quantity of peroxides can cause and already caused [14] rather high destruction effect.

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