OF LIQUID ORGANIC PEROXIDES

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Two methods were developed for determining the relative sensitivity to shock of liquid organic peroxides and peroxide solutions. The first is a modification of the Bureau of Mines drop-weight test in which the amount of gas liberated by the decomposition can be estimated. The potential energy necessary to cause an explosion was considerably less than could be determined by observing damage to the container, indicating that some peroxides are more sensitive than was previously suspected. The second method involves subjecting the sample to shock in an autoclave using a blasting cap. Analyses of the gases given off in both tests indicate that the same products are formed as in normal thermal decomposition. These data and the rate measurements obtained in the autoclave tests indicate that the peroxides decomposed as low-order deflagrations rather than as detonations. A convenient estimate of the sensitivity of a peroxide can be made by determining the dilution required to make the peroxide insensitive to the maximum energy of the test apparatus. By using such data, it is possible to relate the sensitivity of a compound to sensitivities of known commercial peroxides.

ORGANIC PEROXIDES are among the more hazardous chemicals normally handled in chemical manufacturing and research. In spite of the fact that peroxides of various kinds have been on the market for many years and have caused considerable damage to both plant and personnel, there is, as yet, no generally accepted set of tests or specifications which can be used by the supplier or user to estimate the hazards involved in the handling of specific peroxides.

As a class, organic peroxides are relatively low power explosives. The yield of gaseous products per mole of peroxide is low compared with that of conventional explosives such as RDX or TNT (3). Further, the heat liberated per mole of peroxide is about 80 kcal. (based on data obtained in these laboratories by high-temperature calorimetry) compared with 104 kcal. for compounds such as lead azide. Peroxides are hazardous, however, because of the extreme sensitivity of certain types to shock, spark, and other forms of accidental ignition (4). Many of the peroxides handled in a routine manner in the average chemical laboratory are far more sensitive to shock than most primary explosives.

Some work has been reported on the adaptation of methods used for testing explosives to the study of hazardous chemicals, such as peroxides (7). In addition, a number of studies on the explosibility of various H_2O_2 mixtures have been reported by Shanley and coworkers (8). Bowden and Yoffe (2) ascribed the initiation of decomposition in liquids by impact to adiabatic compression of air bubbles resulting in hot spots. If these hot spots are of sufficient size, they will grow to explosions. More recent work on liquid propellants by Griffin (δ) shows that impact sensitivity is, in certain cases, a function of bubble volume and that the potential energy at which the probability of explosion is 50% is a function of temperature, which varies according to the Arrhenius equation. The impact test in Griffin's work was highly instrumented. A piezoelectric force transducer and oscilloscope were used to measure the rate of decomposition of the compounds.

Most of the published data on the sensitivity of peroxides resulted from tests which involved subjecting a confined sample of the compound to impact or severe shock from a blasting cap and studying the effect of the resulting explosion on the container used to confine the sample. In the present work, the explosions were studied by the amount and rate of gas evolution during the explosions.

The purpose of the present work was to obtain a reliable testing procedure for evaluating the relative sensitivity of liquid organic peroxides and peroxide solutions, and to obtain sufficient data about the nature of peroxide explosions to facilitate the design of equipment capable of handling these sensitive compounds with minimum hazard.

Materials

Most of the peroxides used in these studies were commercial samples which were used without further purification. Lauroyl peroxide, *tert*-butyl peroxybenzoate, *tert*-butyl peroxyisobutyrate, benzoyl peroxide, *tert*-butyl peroxyacetate, and acetyl peroxide were obtained from the Lucidol Division, Wallace and Tiernan Co. Di-*tert*-butyl peroxide was obtained from Shell Chemical Corp. Diisopropyl peroxydicarbonate was synthesized by reaction of isopropyl chloroformate with aqueous sodium peroxide by the procedure of Strain and coworkers (9).

Drop-Weight Test

Apparatus. The apparatus generally used for testing the impact sensitivity of small samples of materials involves the use of a dropping weight which falls on a piston resting on a hardened anvil. The sample is placed between the piston and the anvil and is thus exposed to the entire impact of the dropping weight. The most common form of this apparatus, developed by the Bureau of Mines, is designed primarily for use with solid explosives. The explosive is confined in a metal cap, and evidence of explosion is the sound of the report or the damage done to the cap. To study liquid solutions, it was necessary to modify this apparatus considerably. The impact tester used in this work is shown in Figure 1. Details of the piston and sample holder are shown in Figure 2.

The sample is contained in a small brass cap which makes a press-fit on the end of a piston. The piston rests on a hardened steel anvil and is surrounded by a steel ring which encloses the apparatus in a nearly gas-tight fit. The ring has a tube fitting connected to the gas buret by Tygon tubing. The whole assembly is surrounded by a metal shield during testing. This shield acts as a safety support for the weight when the apparatus is being assembled for testing. The weight can be dropped from any height up to 30 inches. When it hits the piston, a catch is released which stops the weight at the height of its rebound, thus preventing multiple impact. The entire apparatus is mounted on a heavy steel column bolted to a concrete slab.

Procedure. For a test, 40 mg. of sample is placed in a brass cap. The piston is then forced into the mouth of the cap and the whole assembly placed on the anvil through the guide and gas-retaining ring. During this operation the guard is up and the weight (15 lb.) is resting on the guard. The weight is then raised to the desired height and the guard dropped in place. The styrene foam rider in the gas buret is placed at zero, and the weight is dropped. If no explosion occurs, the position of the rider in the gas buret will change by less than 0.4 cc. A larger change is an indication of the evolution of gas during decomposition. By placing a gas sample bottle in the line between the ring and the gas buret, it is possible to obtain a sample of the gas given off during the decomposition.

The conventional "up and down" experimental design (5) was used in testing benzoyl peroxide and RDX to standardize the impact tester and to establish a relative scale for comparing it with other impact testers. Benzoyl peroxide had a median drop height of 6 inches and RDX a median drop height of 20 inches. These correspond to 90 and 300 inch-pounds of energy, respectively.

The up and down design works satisfactorily for most solid peroxides but has not been found reliable in this work for liquid peroxides. Tests with liquid peroxides showed that a median drop height would be established and then drift to some higher or lower value. This may have been due to such factors as slight changes in temperature, the amount of air trapped between the sample and plunger, or the amount of gas dissolved in the liquid (1). To overcome this difficulty, impact tests with liquid peroxides were carried out at the maximum drop height (30 inches), and the concentration of the solution was varied to find the concentration at which the peroxide became insensitive. All concentrations were on a weight by weight basis and were usually determined by titration of the iodine liberated from KI solutions with sodium thiosulfate. At least 10 tests were carried out at each concentration. The amount of gas liberated was determined as a function of peroxide concentration. Only those tests in which decomposition occurred

Holding and release mecha-A. nism for dropping weight Β. Drop height indicator Guides for dropping weight D. Buret for measurement of gas evolved E. Dropping weight F. Piston Hardened anvil G. H. Base



Figure 1. Modified impact tester



were used to determine the average amount of gas liberated. Partial decomposition may occur simply from the temperature increase caused by the energy of impact.

Results. Figure 3 shows the effect of concentration on the amount of gas evolved from impact tests of *tert*-butyl peroxy-acetate and *tert*-butyl peroxybenzoate. The former was sensitive at a lower concentration than *tert*-butyl peroxybenzoate. Both reached maximum decomposition in this test over a fairly narrow range of concentrations, and there was considerably more gas evolved from the decomposition of the peroxyacetate than from the peroxybenzoate. This figure gives an indication of the concentration of peroxide likely to be insensitive.

A probability plot (arithmetic probability paper) for the decomposition of *tert*-butyl peroxyacetate and *tert*-butyl peroxybenzoate is shown in Figure 4. A probability of 1 indicates that the sample will decompose on every trial, whereas a probability of 0.5 indicates that half of the trials will result in decomposition. The liberation of more than 0.4 cc.



0.99 0.99 0.00

of gas during a test was defined as decomposition. Ten tests were carried out at each concentration. Assuming that the same distribution occurs in the extrapolated range, the straight line obtained in this probability plot may be used to estimate the probability of decomposition for concentrations of peroxide which would be impossible or impractical to test because of the large number of tests required to establish the probability.

Temperatures which occurred during deflagrations were usually considerably lower than those occurring in detonations, where temperatures are usually in the range of 2000° to 5000° C. At the higher temperatures of detonations, most organic molecules break down into simple molecules such as CO, CO₂, H₂, and other elemental fragments. In these impact tests, the gases obtained were, for the most part, the same as those obtained in normal thermal decomposition and not those expected from a detonation. For example, the only gaseous product obtained from the impact test on benzoyl peroxide was CO₂, which is also the major gaseous product in normal thermal decomposition (10).

The relative sensitivities of various peroxides are shown in Table I, in which the peroxides are listed in order of increasing sensitivity. Lauroyl peroxide was one of the least sensitive peroxides tested, and acetyl peroxide was the most sensitive.

Closed-Vessel Test

Apparatus. The closed-vessel test is a more stringent test devised for determining the shock sensitivities of larger amounts of peroxides and for measuring their rates of decomposition. Figure 5 is a schematic diagram of the apparatus. In this test, a 20-ml. sample of the compound to be tested was placed in a polyethylene beaker in the center of a 250-cc. autoclave. A No. 6 blasting cap, wrapped in polyethylene

Table I.	Critical	Concentrations	of	Various	Peroxides
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	Concn., Wt. %		
Peroxide	Closed- vessel	Impact	
Lauroyl peroxide Di-tert-butyl peroxide tert-Butyl peroxybenzoate Diisopropyl peroxydicarbonate tert-Butyl peroxyisobutyrate tert-Butyl peroxyacetate Benzoyl peroxide Acetyl peroxide	>99 91 71 54 50.5 45.8 <50 20	>99 >97 71 78.4 50.5 58.5 <50 >25	

film and wired to a bell transformer, was immersed in the sample in the beaker. The autoclave was equipped with a pressure gage, which was protected from shock by a valve, and with a pressure transducer, which was attached by a 1/s-inch-diameter line to the autoclave head. (This line was not filled with fluid; however, there was no evidence of spurious pressure waves.) The output from the transducer was fed through a vacuum tube voltmeter (for amplification) to a Sanborne recorder. The autoclave was placed behind a concrete barricade, and flushed with nitrogen during a pre-liminary pressure test.

Procedure. To start the test, the Sanborne recorder was turned on; then the blasting cap was ignited by application of 6 volts a.c. from the bell transformer. After the transient pressure changes were complete, the Sanborne recorder was turned off, the valve opened to the pressure gage, and the residual, or equilibrium, pressure in the autoclave recorded. The gas was then vented through a gas sample holder and analyzed. In later work, the recording system was replaced. A Norwood Controls pressure monitor, which provides calibration and amplification of the output from the transducer, was connected to a dark trace cathode ray tube recorder Storascope (Wandel and Goltermann), which allows the sweep image to be retained until it is deliberately erased.

The time required for a decomposition to reach one half its maximum pressure was measured and designated $T_{1/2}$. This time is an indication of the rate of decomposition of the peroxide under these conditions and at the temperature of the deflagration. This time varied from 5 to 1250 milliseconds for the peroxides tested. The residual pressure in the autoclave, after temperature equilibrium was reached, was measured by opening the valve to the pressure gage. This equilibrium pressure indicated the degree of decomposition which had occurred, since it is a measure of the permanent gases liberated at the temperature of the autoclave. Based on the amount of permanent gas liberated and with certain assumptions about the number of moles of products which would be volatile at the explosion temperature but not at the equilibrium temperature of the autoclave, it is possible to estimate the approximate temperature of the gases formed initially in the explosion by using the ratio of the instantaneous to the equilibrium pressures recorded. During decomposition, the temperature at maximum pressure (750 p.s.i.) for di-tert-butyl peroxide at a concentration of > 97% is approximately 710° C. The temperature of tert-butyl peroxybenzoate (1500 p.s.i. and > 95% concentration) is approximately 720° C. This is further evidence that the peroxides are decomposing by deflagration rather than by detonation.



Figure 5. Schematic diagram of closed-vessel test

Results. The maximum pressure and $T_{1/2}$, as recorded by the Sanborne recorder, increased as the size of the charge increased (Table II). In Figure 6, the effect of mixing the peroxide with an equal weight of dimethyl phthalate is shown by the increase of $T_{1/2}$ from 26 to 110 milliseconds. In Figure 7, the pressure rise and $T_{1/2}$ for di-*tert*-butyl peroxide is shown as recorded by the Storascope. The velocity of the deflagration of di-*tert*-butyl peroxide is much faster than that found for benzoyl peroxide.

The equilibrium pressure for various concentrations of *tert*butyl peroxybenzoate in the closed-vessel test is shown in Figure 8. The curve is similar to that found for the compound during the impact test but is displaced to a lower concentration, as expected, because of the greater shock involved in the closedvessel test.

The gaseous products from the decomposition of various peroxides are shown in Table III. The gas from the autoclave was vented through gas sample bottles and analyzed by gas chromatography. The gaseous products obtained in the closed-vessel test are similar to those found as a result of thermal decomposition (9), which indicates that the temperatures during decomposition in the closed-vessel test were fairly low.

A series of tests was carried out on the peroxides listed in Table I to determine their critical concentrations by the closed-vessel test. The critical concentration was defined as the highest concentration found to be insensitive in five successive tests. This was done by running tests at successively lower concentrations, cleaning out the autoclave, and recharging it between each test, until no decomposition occurred. Four more tests were then carried out at this level to ensure the reliability of the results. The order of sensitivity in the closed-vessel test was about the same as that found in the impact test.



It must be emphasized that this test should not be run with compounds known to detonate, since serious damage could result to the apparatus and ancillary equipment. For this reason, in the present work the closed-vessel test was run only after the compositions had been checked in the impact machine.

Conclusions

The two tests described may be considered to be complementary. The impact test may be used with small quantities of peroxides to estimate their sensitivities. A more complete evaluation then may be carried out in the closed-vessel test using larger amounts. The impact test is particularly useful as a research tool, since it makes available a reliable shock test on a scale sufficiently small that no undue hazards are involved in synthesis or testing of the compound.

Table II. Effect of	Sample Size on De Peroxide	eflagration of Benzoyl
Weight of Peroxide, Grams	Maximum Pressure, P.S.I.G.	T _{1/2} , Msec.
5 10 20	400 750 2400	20 26 40

Table III. Gases from Decomposition of Two Peroxides

	Amount of Gas Liberated, $\%$					
	Benzoyl F	Peroxide	Diisopropyl Peroxydicarbonate			
Gas	Heating	Closed- vessel test	Heating	Closed- vessel test		
CO2 CH4 C2H6 C3H8 Others	100 0 0 0	100 0 0 0 0	$82.0 \\ 0 \\ 14.2 \\ 0 \\ 3.8$	71.5 4.8 15.7 0 8.0		

The decompositions of the peroxides studied in this work are believed to be deflagrations, rather than detonations, for the following reasons: The temperatures, as calculated from the instantaneous pressure rise, were about 700° C.; much higher temperatures would be expected from a detonation. The pressures generated were low compared with those generally found in a detonation; detonation pressures are usually about 1,000,000 p.s.i. or higher, and deflagrations are usually 50,000 p.s.i. or lower. The gaseous decomposition products obtained during these tests were similar to those obtained during normal thermal decomposition and did not show the extensive breakdown into more elemental components one would expect from a detonation.

It should be emphasized that the tests described do not estimate the safety of a peroxide for a given application. This can be determined only on the basis of experience in the shipping, handling, and storage of such chemicals and involves many factors in addition to shock sensitivity. It is obvious from the data presented that dilution of a peroxide with a suitable solvent will reduce the shock sensitivity to almost any desired level. Standards have been set up in the industry, based on existing tests and experience, for shipment and storage of peroxides either in the pure form or suitably diluted (7). It is, however, the opinion of the authors that previous test procedures used with peroxides were not sufficiently sensitive to detect the low-order deflagrations which occur in diluted peroxide solutions and that, as a result, the hazards involved in their use have often been underestimated. Since it is likely that many explosions caused by peroxides start as low-order deflagrations and propagate into higher order deflagrations or detonations, it may be advisable to re-evaluate the significance of peroxide sensitivity measurements.

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