NOMENCLATURE

$a_{\pm}$ = mean ionic activity
A = constant in Debye-Hückel equation
B = constant in Debye-Hückel equation
I = total ionic strength of Lewis and Randall
K_H = hydrolysis constant
K_w = ionization constant of water
K_2 = second ionization constant of sulfurous acid
ln = natural logarithm
m = molality, moles/1000 grams of solvent
x = degree of hydrolysis—the fraction of the sodium sulfite that is hydrolyzed
γ = mean ionic molal activity coefficient

Subscripts

1 = refers to sodium sulfite
r = refers to dilute solution used for lower limit of integration in Equation 1
R = refers to sodium chloride reference solution

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Explosion Limits of Liquid Systems Containing Hydrogen Peroxide, Water, and Oxygenated Organic Compounds

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STUDIES on the explosive limits at room temperature of hydrogen peroxide–water systems containing methanol (*4*), ethanol (*4*), or glycerol (*4, 8*) show that the regions of unstable compositions are well defined. In this investigation, an attempt has been made to assess the effect of such factors as temperature and type of initiation on mixtures of hydrogen peroxide and water with various organic compounds such as 2-propanol, all of which are soluble in hydrogen peroxide. As yet the effect of temperature has not been described in the literature.

Several types of initiation are described—impact, blasting cap, and a high velocity shock wave.

For some compositions, the over-all reaction between the organic materials and hydrogen peroxide can proceed at a rate such that a stable detonation wave is propagated through the liquid. Near the limits determined by impact or blasting cap, however, the reactions are more nearly characteristic of rapid deflagration or explosion than of sustained detonations. In all of these instances, the force of the reaction is sufficient to lead to the destruction of containers and considerable damage to the surroundings. A knowledge of the explosion boundaries will thus define the limits of safe operation or safe handling of mixtures of hydrogen peroxide and organic compounds. These boundaries have been well defined for many systems and may be easily determined by a simple impact test for others.

METHODS OF MEASUREMENT

Impact Tests. Two types of impact testers have been used during the investigation. The simpler of these is a modification of the test apparatus described by Bellinger (*1*).

The piston and cylinder (1⅜ and 1 inch long, respectively, and 0.3 ± 0.0002 inch in diameter, lapped to fit) were of hardened tool steel for greater reproducibility of the impact shock. Straight pins without enlarged heads were less susceptible to breakage but required a guide pipe to center the striking blow delivered by a 360-gram weight falling from a height of 180 cm.

The more complicated apparatus shown in Figure 1 was designed to study the effect of higher temperatures on the explosion limits. A 500-gram weight falling 200 cm. drives the piston into the chamber containing the test solution with approximately 50% greater energy than the first tester. The steam jacket around the cavity allows the attainment of elevated temperatures (within 20 to 30 seconds) just prior to the moment of impact. The packing gland prevents evaporation from the hot sample.

Both instruments were designed with a small cavity or

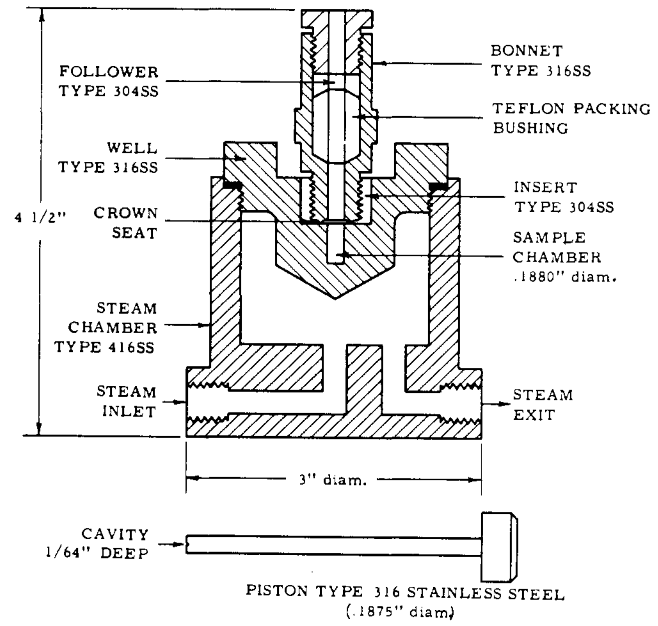

Figure 1. Impact tester II

depression in the end of the piston ($\frac{1}{16}$ inch in diameter and $\frac{1}{16}$ inch deep) to ensure the entrapment of a gas bubble prior to the impact upon the liquid. The work of Bowden and others (*2*) showed that the presence of a bubble (as small as 10^{-7} cc.) rendered liquid explosives, such as nitroglycerin, detonable by a very gentle impact (20 gram-cm.); in the absence of these minute bubbles, potential energies as high as 10^5 to 10^6 gram-cm. were required for detonation.

The results obtained with the two types of impact apparatus were usually in good agreement. A positive test was judged by the rebound of the weight or the appearance of carbon on the piston. The test was done 10 times on each sample, and a single positive result was considered as proof of an explosive mixture.

Cap in Pipe Test Method (*8*). A 10-cc. sample in a glass test tube was subjected to the shock of a No. 6 blasting cap immersed in the liquid. The intensity and sharpness of the sound and the brisance of the explosion as shown by the fragmentation of the thick-walled lead pipe enveloping the sample were compared with a blank of 90% hydrogen peroxide. The presence of any residual liquid indicated that the mixture would not lead to a propagating explosion and, therefore, was considered a negative test.

Shock Wave. The third method for initiating explosion was by means of a high energy shock wave (*7*).

A 1- to 4-liter sample was placed in a cylindrical tube on top of a 2-inch-thick block of Composition B explosive, which has a detonating pressure of approximately 270 kilobars. The Composition B pad was initiated with a plane wave generator. The resulting reaction wave in the explosive charge was followed by means of a synchronized high speed photographic technique as it traveled through the peroxide solution. Steady detonations were observed for some solutions, failing detonations which proceeded more than 3 inches into the solutions were observed for others, and some displayed no reaction wave beyond the point at which a luminous wave was observed in a blank of water (2 or 3 inches from the surface of the initiator).

LIMITS OF EXPLOSION

Effect of Temperature. The limits of explosion for the 2-propanol–aqueous hydrogen peroxide mixtures were measured by impact test at 21° and 133° C., using the second tester described above. Additional data obtained by the simplified impact tester and the blasting cap tests are shown with the former in Figure 2 for comparison. Also shown are the limits calculated from the heats of reaction and vaporization (*11*).

At 21° C. for the system 2-propanol–hydrogen peroxide–water, the explosion regions determined by these two test methods were about the same, especially with mixtures of low organic content. Some widening of the area by the cap method is indicated in the region of high-organic concentration but is not conclusive because of the lack of tests in this region.

Increasing the temperature of the system to 133° C. resulted in a possible small widening of the limits of explosion as measured by impact test (Figure 3).

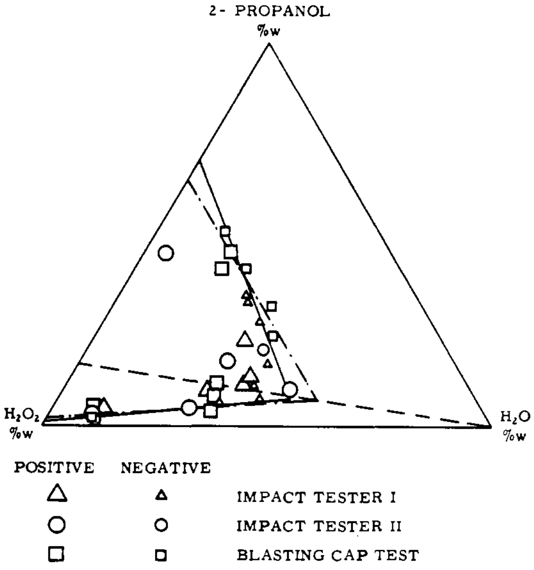

Figure 2. Explosion limits for liquid system 2-propanol–hydrogen peroxide–water at 21° C.

————Calculated limits

·············Stoichiometric composition

—·—·—Shanley and Perrin method, 0.8 kcal. per gram

Effect of Diluent Acetone. The effect of acetone was determined by employing a solution of 25% weight acetone and 75% weight 2-propanol as the organic component in the impact tests (Figure 4). Acetone was chosen as the diluent largely because its energy content is similar to that of 2-propanol, yet it is more stable with respect to oxidation.

The area of explosive compositions at 21° C. is possibly slightly greater, as expected, than that for the 2-propanol system, except at the apex or high water concentration region. Mixtures in this concentration region were singularly difficult to explode by impact and the boundary is not sharply defined.

At 133° C. the experimental explosions for the mixtures in the high water concentration and organic-rich regions more nearly agree with the calculated boundary. The fact that differences occur at high organic or high water concentration and not at high peroxide concentration suggests that variations in types and rates of chemical reaction and incomplete combustion are responsible.

EFFECT OF HIGH ENERGY INITIATION

Figure 5 shows the results of the tests with initiation by high energy shock waves. In some samples, the detonation wave from the initiator propagated at constant velocity (or increasing velocity) through the full length (12 to 15 inches) of the sample; these are labeled "steady detonations."

In the region of high peroxide concentration, the agree-

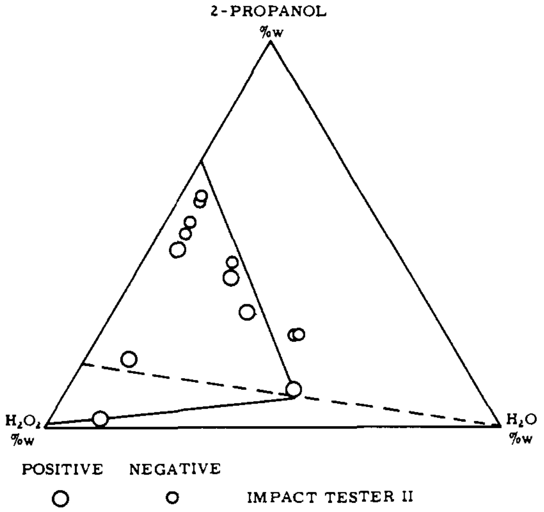

Figure 3. Explosion limits for liquid system 2-propanol–hydrogen peroxide–water at 133° C.

———Calculated limits
-------------Stoichiometric composition

ment with the impact test data is excellent. The separation between steady detonation and nondetonation is sharp. With more water present only failing detonations were observed. Compositions giving this result fell within the explosion limits determined by impact tests. With 35% water present, not even failing detonation could be observed.

Three mixtures of peroxide, water, and ethanol detonated by Haeuseler (*4*) are included in the figure for comparison.

EXPLOSIONS WITH OTHER OXYGENATED ORGANIC COMPOUNDS

Several other oxygenated organic compounds have been mixed with hydrogen peroxide and water and tested by the impact and blasting cap (Table I).

Table I. Explosion Boundaries of Organic Compounds in Concentrated Hydrogen Peroxide

(By impact tester I)

Organic Compound	Composition, Wt. % Org.	H_2O_2	H_2O	Explosibility	Efficiency, Explosions/Impacts
Methanol	8.4	82.4	9.2	+	4/10
Formaldehyde	7.7	71.7	20.6	–	0/10
	12.0	61.4	26.6	+	4/10
Acetaldehyde	2.7	88.5	8.8	–	0/10
	6.2	84.4	9.4	+	2/10
	9.0	82.6	8.4	+	9/10
Formic acid	5.3	84.5	10.2	–	0/10
	9.9	80.4	9.7	–	0/10
	14.9	75.2	9.9	–	0/10
Acetic acid	12.1	71.2	16.7	–	0/10
	14.2	69.4	16.4	–	0/10
	15.0	68.9	16.1	–	0/10
	17.2	67.1	15.7	–	1/3
	18.2	66.2	15.6	+	1/1
	20.3	55.3	24.4	–	0/10
	23.3	53.3	23.4	+	2/10

Only a few concentrations of each organic compound have been tested. However, with the exception of formic acid, the explosion limit has been located to within a few per cent. The aldehyde can be tolerated safely at slightly higher concentrations than the alcohols. Up to 15 weight % solutions of the acids, freshly mixed, are apparently safe.

In Table II the results of the blasting cap tests on solutions of these compounds are given. Considerably less organic material was needed to give positive explosions than would be indicated by the results of impact tests. It is presumed that the impact tester (an early model of tester I) used to obtain the data in Table I was not as efficient as the later model.

No positive explosions were observed outside the calculated composition boundaries and only two negative points are located inside these boundaries. For the alcohols and aldehydes these boundaries are believed to be conservative estimates of the explosive compositions.

For acetic and formic acid solutions in hydrogen peroxide the data given are correct only for freshly mixed solutions.

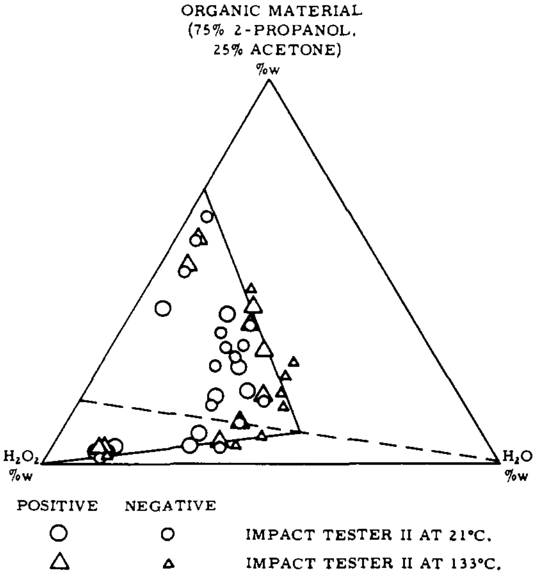

Figure 4. Explosion limits for liquid system 2-propanol–acetone–hydrogen peroxide–water

——Calculated limits
--------Stoichiometric composition

Table II. Explosion Boundaries of Organic Compounds in Concentrated Hydrogen Peroxide

(Blasting cap tests)

Organic Compound	Composition, Wt. % Org.	H_2O_2	H_2O	Explosibility	Degree of Decomposition
Methanol	1.7	88.7	9.6	–	Partial
	3.3	87.0	9.7	+	Complete
	6.2	84.0	9.8	+	Complete
	6.1	69.7	24.2	Borderline	Partial
	7.2	69.7	23.1	+	Complete
Formaldehyde	5.1	77.7	17.2	–	Partial
	6.8	73.7	19.5	+	Complete
	8.0	70.8	21.2	+	Complete
Acetaldehyde	2.3	87.9	9.8	–	Partial
	3.3	86.9	9.8	+	Complete
	6.5	84.1	9.4	+	Complete
	5.0	69.8	25.2	–	Partial
	6.1	69.7	24.2	Borderline	Partial
	8.0	69.8	22.2	+	Complete
Propionaldehyde	2.3	87.9	9.8	–	Partial
	3.4	86.9	9.7	+	Complete
	5.0	69.7	25.3	–	Partial
	6.2	69.7	24.1	Borderline	Partial
	7.3	69.7	23.0	+	Complete

No positive tests were observed with the freshly mixed formic acid–peroxide solutions and these tests, as well as the acetic acid tests, are in agreement with the calculated curves.

EFFECT OF TIME

On standing, organic acids and hydrogen peroxide react to form the monoperoxy organic acids. Table III gives the results of tests made with formic and acetic acid solutions in hydrogen peroxide and water after standing at room temperature for 8 hours. Mixtures well outside the calculated boundary for the unreacted acids are now shown to be explosive. Although the explosive boundaries for equilibrium mixtures of the peroxy acids could undoubtedly be determined experimentally, it is obvious that thermodynamic data for the three-component systems cannot be used to predict the behavior of the newly formed four-component systems. Any catalyst present would constitute another component and might further invalidate the method of prediction. Since partial oxidation to peroxy acids can occur with other organic compounds as well over longer periods of time, the only safe procedure is to test peroxide solutions experimentally under the same conditions as those under which the peroxide solutions are to be used. A more detailed discussion of ways in which explosive mixtures may be found has been published (*10*).

Table III. Explosion Boundaries of Organic Compounds in Concentrated Hydrogen Peroxide

Composition of Mixture, Wt. %			Time after Mixing, Min.	Temp., ° C.	Cap Test Explosibility
Org.	H_2O_2	H_2O			
Formic acid					
			3	24	–
15.5	73.9	10.6	30	24	+
			300	24	+
			2	15	–
19.8	69.4	10.8	300	0	–
			480	0	+
			4	21	–
			14	21	–
			49	21	+
			104	21	+
			3–5	35–38	–
			8–10	35–38	+
			15–25	35–38	+
			4	15–20	–
30.1	49.8	20.1	30	15–20	Borderline
			90	15–20	+
			480	15–20	+
			480	15–30	–
15.1	49.7	35.2	400	25–35	Borderline
11.0	78.6	10.4	350	18–35	–
5.5	81.9	12.6			
Acetic acid					
			350	35	–
2.9	87.5	9.8	40	27	–
4.3	86.1	9.6	3	31	–
6.4	84.2	9.4	13	30	+
			510	15–30	–
6.1	69.8	24.1	4	16	+
10.1	69.8	20.1	480	15–30	+

EFFECT OF VOLUME

It is obvious from the definition of a positive cap test that mixtures, which are only partially exploded in 10-cc. samples, might be completely exploded in smaller samples, or that mixtures which are just on the boundary and are completely exploded in 10-cc. samples might be only partially exploded in larger samples. The results of tests on various sample sizes from 5 to 4000 cc. bear out these suppositions. Samples of 5-cc. volume were completely destroyed, while 10-cc. samples of the same composition were only partially exploded. Figure 5 shows that samples distinctly positive by blasting cap and impact test failed to support a detonation wave more than a few inches through the solution. Mixtures of greater organic and greater water content have also shown this failure to sustain the shock wave through larger volumes of solution. However, mixtures of high peroxide content and organic concentrations only slightly greater than the limits defined are capable of propagating the initiated reaction through volumes of 1 gallon or more. The reaction can be a steady detonation in rich fuel-peroxide mixtures.

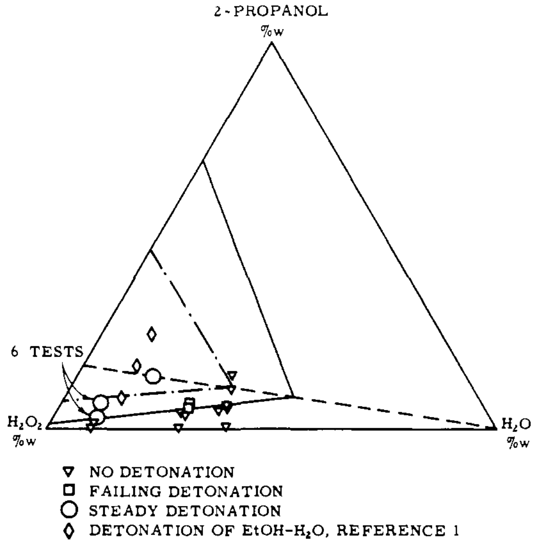

Figure 5. Detonation tests by shock wave initiation

——Calculated explosion limits

--------Stoichiometric composition

--------Shanley and Perrin method, 1.1 kcal. per gram

DISCUSSION

The propagation of a detonation wave through a liquid depends, essentially, on the rapid release of the proper amount of energy from the reaction occurring at the wave front. For the organic compound–hydrogen peroxide–water systems reported here, the amount of energy available to sustain a reaction wave front depends not only on the peroxide-organic ratio but also on the amount of water present which will absorb the energy and hinder the reaction. There are, therefore, both minimum and maximum limits, which define the amount of organic material required and the maximum limit of water which can be tolerated in order to sustain or propagate a detonation wave. Outside these limits other limits of composition define solutions in which the energy release is sufficient to support an initiation wave of some specific strength through a solution volume of some specific size. The choice of the strength of the initiator and the solution volume is somewhat arbitrary.

To be consistent with previous investigations, the initiation energy used to define these latter limits was the No. 6 blasting cap in 10 cc. of solution. Close within these concentration limits are regions of composition which may be exploded by impact shock. The energy applied by the latter is of the order of 20 to 80 gram calories per gram of solution exploded compared to 100 to 200 gram calories provided by the blasting cap test and considerably less than the energy released by the reaction (greater than 400 gram calories per gram of solution exploded).

How great a quantity of solution of borderline composition could be exploded by the impact shock is not known. In all probability, it would vary, depending on the region of composition and the shape of the charge. With high organic water content the reaction would probably decay in a short time. In the region of high peroxide concentration, the reaction might be a steady detonation.

The concentrations of mixtures of peroxide and organic material which undergo steady detonation maintain detonation velocities as high as 6500 meters per second. This compares to the high velocity detonation of 7700 meters per second reported for nitroglycerin (*5*). Similar velocities (up to 6700 meters per second) and steady detonations of lower velocity, comparable to the low velocities reported for nitroglycerin, were observed for the system ethanol–hydrogen peroxide–water (*4*).

The calculated curves shown in the previous figures are based on the energy liberated by the reacting mixtures. In this method, described elsewhere in detail (*11*), account is taken of the available sources of energy and the energy sinks in a given mixture. A composition is at the limit when an excess amount of energy is released, in this case 450 cal. per gram of solution. The choice of 450 cal. per gram has no particular theoretical significance, except that it is the amount of energy liberated by the complete reaction (oxidation of organic compounds and decomposition of hydrogen peroxide) at the explosion limits defined above.

With the exception of the aged acetic and formic acid solutions, the calculated limits fit the experimental data very well. The large number of positive tests made on the 2-propanol–hydrogen peroxide–water system all fall within this calculated limit. This method of calculation would also explain the small effect of the initial temperature of the solution on the positive limits, because the energies of the reactions are relatively insensitive to temperature. Because the initiation of explosion by impact test may well take place by means of adiabatic compression of tiny bubbles of gas at the moment of impact factors such as moderate changes in temperature may affect the explosion limit by changing the composition of the bubbles. Mulcahy (*6*) has found, for example, that the susceptibility of nitroglycerin to explosion by impact is strongly influenced by the chemical nature of the gas present. The effect of the acetone diluent observed in the present work may have appreciably altered the bubble composition compared to 2-propanol alone. Moderate differences in temperature in themselves would probably not be important because of the extraordinarily high temperatures (1000° C.) and pressures (610 atm.) which can occur at the moment of impact (*3*).

The limits calculated for the formic and acetic acid systems cannot fit the data obtained on aged solutions, since the acids have reacted to form a certain amount of the peroxy acids. Therefore, the systems have become quaternary, instead of ternary, and the thermodynamic data used for the calculation are no longer sufficient.

A more simplified method of calculation, ignoring the vaporization of the unreacted components and the products, has been published recently (*9*). A calculation by this method using 0.8 kcal. per gram excess gives a reasonable fit to our experimental data as shown on Figure 2, but compromises the margin of safety in the peroxide-rich region where steady detonations have been observed. The calculation using 1.1 kcal. per gram as suggested by Shanley and Perrin for determining the impact boundary, suggests that certain mixtures are safe which are clearly not so in the light of the present detonation data (Figure 5).

Because of the hazards inherent in organic compound–hydrogen peroxide solutions due to the exposions that are possible and the possibility that chemical changes may bring previously safe mixtures into the explosive region, the limits calculated for such a system should be viewed only as guides for selecting the proper mixtures for further experimental tests. This is true for simple systems, and even more so where a catalyst is present that may modify the system.

The number of negative tests which fall inside the calculated limits, especially in the organic-rich region and in the region of highest water composition, suggest that incomplete combustion occurs there, releasing less energy than is calculated. In this region, in many instances, free carbon was formed during the impact test. Little or no carbon was observed during tests on the mixtures rich in hydrogen peroxide.

CONCLUSIONS

The vigorous tests applied to the system 2-propanol–hydrogen peroxide–water have shown clearly that steady detonations can occur in limited regions of concentrations of the three components. In other regions rapid deflagrations can be initiated. A greater region of concentrations is nonexplosive. Further, a rather simple experimental tool, the impact tester, is capable of defining the limits of possible explosions with a fair margin of safety. Chemical changes taking place on standing or as a result of other added reactants can make a powerful explosive out of an apparently nonexplosive mixture; therefore, careful experimentation should precede the mixing or use of a mixture containing hydrogen peroxide and organic substances.

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