Detonability of the System Nitrobenzene, Nitric Acid, and Water

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The limits of detonability in 1-inch-diameter charges of the system nitrobenzene–nitric acid–water at 25° and 80° C. and benzene–nitric acid at 25° C. were determined. Limited shock-sensitivity measurements were made using the card-gap technique. In general, the limit of detonability of the nitrobenzene system coincided with the region of complete miscibility in the ternary diagram.

THE ABILITY of nitrobenzene and nitric acid to form detonable mixtures has been known for many years (*2*). Cook (*4*) used a mixture of 24% nitrobenzene, 63% nitric acid, and 13% water to study the reaction thickness in detonation. As part of an investigation of liquid explosive mixtures based on nitric acid, Kurbangalina (*7*) studied the explosive properties of a mixture composed of 72% nitric acid and 28% nitrobenzene. The critical charge diameter for this mixture was less than 0.6 mm. in contrast to 2 to 2.5 mm. for nitroglycerin under the same experimental conditions, and the stable detonation rate was 6200 to 6800 meters per second.

In considering the handling of liquid explosive systems, some evaluation must be made of the ease of initiation of detonation by mechanical shock in addition to the compositional limits of detonable mixtures. In recent years, the card-gap technique developed by Pape and Whitbread (*9*) has been used quite extensively (*1, 3, 5, 6, 8*) to evaluate the relative ease of initiation by an explosive shock, under very specific physical conditions of many explosive materials. This work has resulted in the accumulation of a fair amount of semiquantitative experimental data against which new results may be compared to give an evaluation of relative sensitivity to shock initiation (*10*).

In the present investigation, the limits of detonability of the nitrobenzene–nitric acid–water system were determined by the card-gap technique at 25° and 80° C. Within these limits, considerable data were obtained on the effect of composition on sensitivity—i.e., ease of initiation. Since part of the system forms two immiscible liquid phases, the solubility diagram of the three-component system was determined at 25° C. in order to compare the area of detonability with the area in which two phases form. For comparison with the nitrobenzene system, limits of detonability were determined for the benzene–nitric acid system at 25° C.

EXPERIMENTAL DETAILS

The version of the card-gap technique employed in this investigation consists of the following elements:

A donor explosive charge, a variable gap of plastic cards, a container for the sample, and a steel witness plate to indicate whether or not initiation occurs in the acceptor cup. The donor is made up of two 25-gram cylindrical tetryl pellets (1 inch high by 1.625 inches in diameter) whose density is 1.57 ± 0.03 grams per cc. The shock-attenuating barrier or gap consists of an appropriate

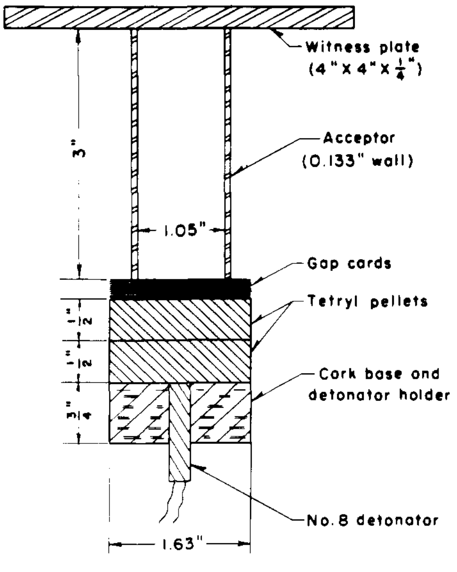

Figure 1. Arrangement for card gap experiments

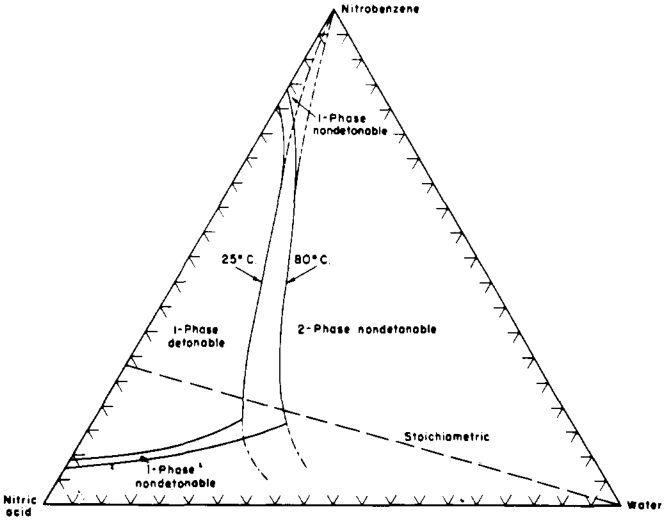

Figure 2. Detonability and miscibility limits in the nitric acid–nitrobenzene–water system at 25° and 80° C. and zero gap
Detonable systems at given temperature are left of the solid lines, nondetonable to the right. Scale in wt. %

number of 0.010-inch-thick cards of cellulose acetate stock. Accurately machined cylindrical blocks of polymethyl methacrylate are substituted for thick stacks of plastic cards when repetitive tests are made at large gap values; the finer gap variations are again attained by adding plastic cards. The container is a 3-inch length of 1-inch, Schedule 40, black steel pipe sealed off at the bottom with polyethylene film. Evidence of initiation of the liquid is provided by a witness plate of cold-rolled mild steel, 4 × 4 × 0.25 inches. The tetryl booster rests on a cylindrical block of cork or soft wood 1.62 inches in diameter and 0.75 inch high, with a 0.280-inch hole along its cylindrical axis into which the detonator is inserted (Figure 1).

In use, the components of the test are carefully aligned, the test liquid is added to the cup, and the witness plate is set in place on the top of the acceptor. After the shot, a positive result is indicated by a clean hole cut through the witness plate. Any other condition of the plate was interpreted as a negative result.

RESULTS

The concentration limits of the detonable mixtures of nitrobenzene, nitric acid, and water at 25° and 80° C. were determined at zero gap. Mixtures yielding two phases were not detonable, and the limits of detonability coincided with the limits of miscibility over a wide portion of the compositional diagram. In confirmation, the limits of miscibility were determined by titrating mixtures of nitrobenzene and nitric acid with water to a faint opalescence, indicative of the formation of a two-phase system. No attempt was made to determine miscibility limits in the region of low nitric acid concentrations. Figure 2 gives both the limits of detonability, under the conditions of the card-gap test, and the miscibility limits. The two limits are seen to be identical over a wide range of compositions.

The shock sensitivity of the binary nitrobenzene–nitric acid system as a function of composition was determined. Figure 3 shows the extreme ease with which mixtures near the stoichiometric composition can be shock-initiated. No attempt was made to determine card-gap values beyond 5 inches because of the decreasing significance of the results at these vary large gaps. For comparison, a similar investigation was made of the sensitivity of the binary benzene-nitric acid system (Figure 4). In this case, an apparent maximum sensitivity value at about a 5-inch gap was obtained for the mixture containing 85% nitric acid. The comparable card-gap value—i.e., the one allowing initiation of normal detonation in nitroglycerin—is about 0.4 inch. Although the real sensitivity of different materials cannot be directly equated to the magnitude of the gap values, the nitric acid systems must be considered quite sensitive. The region of maximum sensitivity of the two binary systems approximated the stoichiometric, or most energetic, mixture as anticipated.

To evaluate the relative sensitivity of various nitrobenzene-nitric acid–water mixtures, a series of trials were made on various mixtures at 1- and 2-inch card gaps. The results are shown in Figure 5.

The card-gap technique, in common with most other empirical tests, yields results that are subject to variation if different test conditions, such as the size of the container or of the donor, are employed. Increasing the diameter of the container or increasing the strength of the booster could enlarge somewhat the area of detonable compositions in the single phase systems. The increase in apparent sensitivity from 25° to 80° C. indicates that further temperature increase would also enlarge the range of detonable mixtures. The rather close agreement between the areas of detonability and miscibility in the ternary diagram indicates that the addition of another component to enlarge the range of miscibility in Figure 2 could increase the detonable range as well.

The desensitization caused by low concentrations of water is quite marked. Thus in the region of stoichiometric compositions, 8% water sufficed to reduce the card-gap sensitivity from > 5 inches to about 2 inches; another 10% water reduced the sensitivity to about the 1-inch level. Such reduced sensitivity is quite out of line with a simple reduction of energy content.

To relate sensitivity and limits of detonability to the potential energy yields that could be expected on detonation from various compositions, the latter were roughly estimated from simple thermochemical considerations; precise computation of these energies did not seem warranted.

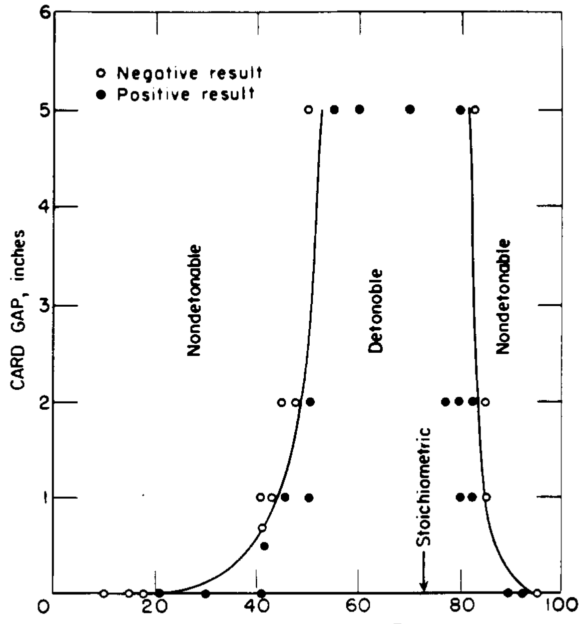

Figure 3. Shock sensitivity studies of nitric acid–nitrobenzene system at 25° C.

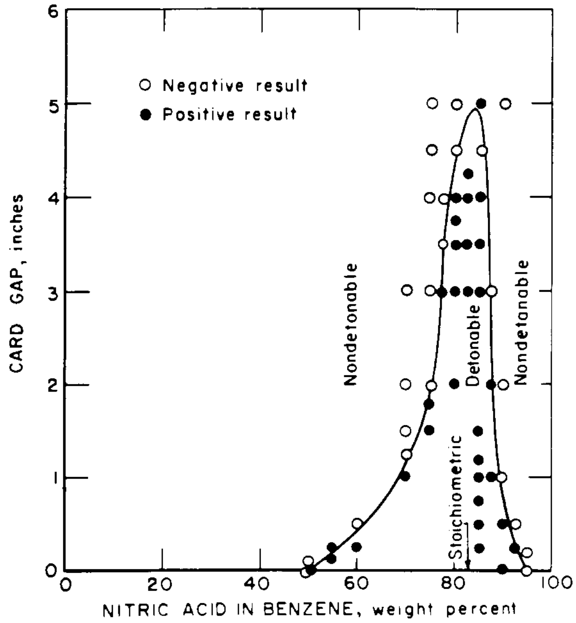

Figure 4. Shock sensitivity studies of nitric acid–benzene system at 25° C.

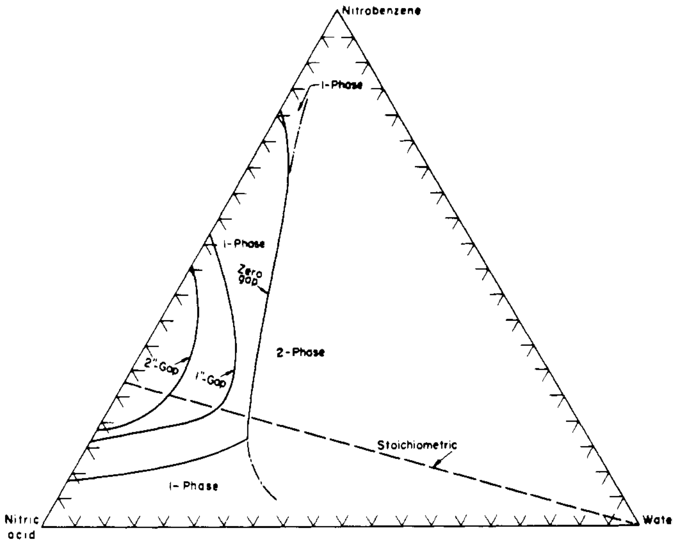

Figure 5. Shock sensitivity of nitric acid–nitrobenzene–water system at 25° C.

Detonable systems at given gaps are left of the solid lines, nondetonable to the right. Scale in wt. %.

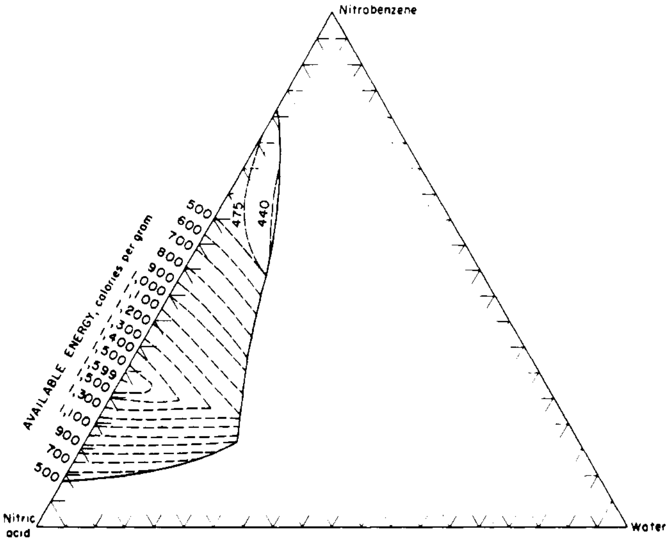

Figure 6. Available energy in the system nitrobenzene, nitric acid, and water at 25° C.

Detonable mixtures are left of the solid curve. Scale in wt. %.

For the reaction $C_6H_5NO_2 + 5HNO_3\ (l) = 6CO_2 + 5H_2O\ (l) + 3N_2$, the liberated energy at 25° C. is about 700 kcal. per gram molecular weight of nitrobenzene. The stoichiometric mixture, 1 mole of nitrobenzene to 5 moles of nitric acid, thus can yield about 1600 cal. per gram of mixture, roughly equivalent to the energy yield from nitroglycerin. For nitric acid-rich mixtures, the liberated energy was estimated by assuming a complete consumption of the available nitrobenzene and correcting the final value for the total weight of the mixture. For fuel-rich mixtures, the liberated energy was estimated by assuming that the reaction proceeds in three steps. Oxidation of carbon to carbon monoxide, and of hydrogen to water are the two initial steps. These are followed by the final oxidation of the carbon monoxide to carbon dioxide. Water in the initial mixtures was treated as a simple diluent—i.e., not equilibrated with carbon in the fuel-rich compositions. On the basis of these assumptions, the available energy has been calculated for various mixtures of nitrobenzene, nitric acid, and water. The results are shown in terms of constant enthalpy contours superimposed on the region of detonable compositions (Figure 6).

The energy content of mixtures lying within the zone of detonability, as so estimated, is seen to be greater than 440 cal. per gram of mixture, to a maximum of about 1600 cal. per gram for the anhydrous stoichiometric composition. That such low-energy liquid systems should be detonable in 1-inch diameter is indicative of quite facile reactivity. In contrast, liquid dinitrotoluene at 200° F. cannot be initiated in 2.5-inch steel pipe with a 240-gram pentolite booster (the critical diameter is on the order of several inches), despite an approximate energy content of 560 cal. per gram.

The addition of water, as shown in Figure 6, has relatively little effect on the computed energy content, in contrast to its effect on sensitivity. This latter effect is most strikingly demonstrated by the abrupt change of high-energy detonable compositions (as high as 1200 cal. per gram) to nondetonable two-phase systems by small additions of water. Clearly, much of the two-phase system, if finely dispersed (emulsified) and in large diameter charges, should be detonable.

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