Reports

Vapor Phase Explosions: Elementary Detonations?

Abstract. Although liquid-vapor explosions are widely observed, there is no established explanation for their initiation and propagation. Thermodynamics admits the possibility that superheated liquids can support detonations analogous to those that occur in chemical explosives. For liquid methane superheated 50 K above its boiling point at 1 atmosphere, the energy of explosion is 2 to 3 percent of that of TNT.

Vapor phase explosions have been observed in numerous industrial and natural situations when hot (perhaps molten) materials have come into sudden contact with relatively cool liquids. In the metal industry many destructive accidents have resulted from accidental spilling of molten metal into water (1). Analogous explosions occur in the paper industry when paper smelt (fused sodium carbonate) is quenched in large containers of 'green liquor'' (1). In the nuclear reactor industry an explosive incident believed to be a vapor phase explosion occurred in a test of the SPERT 1-D reactor in Idaho (1). Liquid natural gas and other light hydrocarbons are observed to explode when poured onto water under certain conditions, and with the advent of large-scale transport of these materials the potential for major catastrophe is of growing concern (2, 3). It has also been proposed that underwater volcanic eruptions, such as Krakatoa, may be accompanied by enormous vapor explosions. The energy release in the Krakatoa eruption is estimated to have been about 200 megatons, for example (4). Finally, vapor explosions have been observed in electrically pulsed wires (5).

In view of the importance of such explosions, it is perhaps surprising that there is not yet a satisfactory explanation for their occurrence. Considerable research has been done, but the experiments reported have not been sufficiently well instrumented to establish the underlying mechanics controlling the ini-



Fig. 1. Liquid-vapor mixed-phase region of methane according to the Redlich-Kwong equation of state. The Rankine-Hugoniot curve centered on the assumed initial state, denoted by a circle, is labeled R-H, the Rayleigh line is indicated by R, the isentrope through the final shocked state is labeled S, T_s denotes the spinodal point on the 170 K isotherm, and CP is the critical point.

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tiation and propagation of such explosions. They have established some important features, however. It is now commonly accepted that vapor explosions require that the initially cool liquid be superheated. Further, they do not require chemical reactions. Beyond these established facts, proposed explanations are usually based on some kind of dynamic mixing hypothesis in which the initiation of the phase change reaction causes enhanced mixing and attendant large increases in heat transfer rates (4).

I suggest here an alternate explanation, namely that the superheated liquid behaves as an elementary explosive and sustains a detonation analogous to those that occur in chemical explosives. A theory for detonations driven by phase changes has recently been formulated (6).

To illustrate the thermodynamic basis for this hypothesis, I have used liquid methane as an example. It is clear from this discussion that detonation is possible; moreover, some parameters of the detonation can be obtained from thermodynamics alone. The major uncertainty regarding this hypothesis devolves on the conditions under which a shock in superheated liquid can be self-initiating.

I have chosen to use the Redlich-Kwong (R-K) equation of state for methane (7). The results are approximate inasmuch as the R-K equation of state does not fit the observed data accurately. However, it is convenient to use and adequate for the present purpose. Refinements to improve the accuracy are straightforward.

The R-K equation is

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)}$$

where P is pressure, R is the gas constant, T is temperature, and v is the specific volume. The parameters a and b are evaluated from the critical point and are given by (7)

$$a = 0.4275 \frac{R^2 T_{\rm c}^{5/2}}{P_{\rm c}}$$
$$b = 0.08664 \frac{R T_{\rm c}}{P_{\rm c}}$$

where T_c and P_c are the critical-point values, 191.1 K and 46.4 bars, respectively.

Figure 1 shows a plot of several isotherms in the liquid-vapor mixed phase of methane. The critical values and other data are from (8). Note that the metastable and unstable portions of the isotherms are shown. The absolutely unstable portions, for which $(\partial P/\partial v)_T > 0$, terminate on the left at the spinodal

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point. This point represents the maximum possible degree of metastable superheating on a given isotherm, and at P = 0 it is about 0.9 T_c. The equilibrium isotherms are horizontal lines in the mixed phase, whose position is determined by equality of the Gibbs potential in the liquid and vapor phases.

For illustration, assume that the material is superheated to the metastable state indicated by the circle in Fig. 1; that is, P = 1 bar, T = 170 K, and $v = 4.0 \text{ cm}^3/\text{g}$. At this point the internal energy is 320 J/g larger than that at the boiling point, 120 K. The Rankine-Hugoniot curve centered here is labeled R-H. Points to the right of the initial volume, v = 4.0, are meaningless and are shown as an aid in locating the curve. A shock centered on the assumed initial state whose end state lies on the equilibrium surface in the mixed phase is seen to be restricted to a narrow pressure range at about 28 bars. Moreover, it represents an eigenvalue, or weak, detonation since the shock is supersonic with respect to the material behind; the isentrope through the final shocked state is shown as the curve labeled S and clearly has a smaller negative slope than the Rayleigh line, labeled R(6).

The detonation velocity cannot be evaluated because it is determined by a saddle-point singularity of the differential equation expressing the relation between the specific volume and the reaction rate in the shock transition (6). It therefore depends on the values of the reaction rate and viscosity coefficients in the final shocked state, and these are not known. The velocity can be bounded below, however, at about 0.5 mm/ μ sec.

The pressure decays in the rarefaction wave following the shock along curve S until the initial pressure is reached. The temperature at that point is 120 K, the specific volume is 178 cm³/g, and the internal energy is 225 J/g. The degree of reaction is 0.45. The difference in internal energy between the initial state for the shock and the final state behind the entire wave is therefore (320 - 225) J/g, or 95 J/g. This energy is extracted as mechanical work and is the effective energy of explosion. It is small, as is the detonation pressure, compared to chemical high explosives, for which the energy is typically 4000 J/g. However, it is sufficient to be very hazardous in large quantities, and seems to be compatible with the magnitude of energy release inferred from observed vapor explosions.

Whether detonations are the mechanism for vapor explosions depends not only on the thermodynamic requirements, which are seen to be satisifed, but

also on the ability of the shock to be selfsustaining. That is, initiation of the reaction must occur in the shock transition laver. On the basis of equilibrium thermodynamics alone it appears difficult to argue that the shock should be self-sustaining. Thus, the effect of the shock pressure is to carry material closer to the equilibrium surface and farther from the spinodal curve.

It may be possible, however, that nonuniform heating in the shock front causes local high temperatures that initiate the reaction, analogous to the situation in liquid chemical explosives. Small bubbles may nucleate in the metastable liquid and have insufficient time to grow before the shock starts. Shock compression of these bubbles can then cause local high temperatures. It may even be unnecessary for bubbles to have formed. Density fluctuations are large in the vicinity of the spinodal point and corresponding temperature fluctuations of the shocked material may be large.

In any case, definitive experiments are required to establish whether the detonation mechanism obtains, as well as to measure pertinent parameters.

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References and Notes

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Head-to-Head Linked Isoprenoid Hydrocarbons in Petroleum

Abstract. A series of petroleum isoprenoid hydrocarbons possessing an unusual head-to-head linkage is present as an important component in petroleum. The entire series appears to be produced by diagenesis or catagenesis from precursors containing 40 carbon atoms. A suitable precursor compound has been reported in one type of living organism, thermoacidophile bacteria.

While high-molecular-weight hydrocarbons possessing a single tail-to-tail linkage, such as squalane (1), perhydro- β -carotene (2), and lycopene (3) have been reported, all other high-molecularweight isoprenoids found to date in fossilfuel samples possess only head-to-tail linkages (4). We now report the discovery of head-to-head linked isoprenoid hydrocarbons of high molecular weight in crude oils. This type of linkage was only recently discovered in living organisms (5).



The solid peaks in Fig. 1 depict the head-to-head linked isoprenoids in considerable concentration (0.1 percent of crude) relative to their head-to-tail linked counterparts (shaded peaks).

The head-to-head linkage was discovered by interpretation of capillary gas

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chromatography-mass spectrometry (GC-MS) (Fig. 2B) of the branched acyclic saturated fraction produced by alumina-silica chromatography (6), with subsequent thiourea adduction (2) from a California Miocene crude. The diagnostic series of ion doublets (7) observed at m/e 112-113, 182-183, 252-253, 308-309, 378-379, and 448-449 (Fig. 2B) is indicative of head-to-head linkage, and confirmation was obtained by comparison with authentic head-to-head iC_{19} - iC_{19} (*i*, isoprenoid) (Fig. 2A).

Authentic 2,6,10,14,17,21,25,29-octamethyltriacontane (1, iC_{19} - iC_{19}) was synthesized in three steps starting from methylpristanate (Analabs). Lithium



aluminum hydride reduction of the ester to pristanol was followed by conversion to 1-bromopristane by means of phos-

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