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ABSTRACT

Application of high pressures can give rise to explosive decomposition of various materials. Possible reasons for this phenomenon are discussed.

ON THE SPEED OF REACTIONS AT HIGH PRESSURES*

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More than twenty years ago Bridgman found that some chemically stable compounds suffer explosive transformations at pressures of several times 10,000 atm[1]. Bridgman applied in his experiments a considerable shear. Under normal conditions the shear strain would have quickly exceeded the elastic limit and no great shear stress could have been established. But at high pressures the elastic limit is greatly increased and considerable shear strains can be established.

Recently experiments have been carried out with sugar,[2] which in Bridgman's experiments had given negative results. In these experiments sugar was exposed to a pressure of several times 10,000 atm and was explosively decomposed at various temperatures. While shear stress has not been applied in as pronounced fashion as in Bridgman's experiments, there are indications that no explosion occurs if the pressure is purely hydrostatic.

In the following, possible explanations for these explosive phenomena are discussed. Actually, several explanations are possible, and more detailed experiments may be needed in order to find the relevant mechanism. We shall consider the explosion of sugar as our main example.

From the point of view of the energy balance, the explosion of sugar is not too surprising. The transformation of sugar into carbon and water releases per unit weight 55% of the energy that is liberated in a TNT explosion. The problem is in what manner the high pressure creates the conditions for the explosive decomposition.

A detonation may occur if the energy produced in the reaction will raise the temperature to a sufficient level. The temperature is sufficiently high if it will permit the neighboring molecules to react before the local energy has been transferred by the sonic (or supersonic) process to a bigger portion of the substance, thereby lowering the temperature below the point at which the explosion can proceed. While these ideas can be formulated in a quantitative manner,[3] for our discussion the qualitative approach will suffice.

High pressure may aid the explosive process by making a greater fraction of the energy available for local reactions. At 50,000 atm the value of pV is comparable in solid sugar with the energy of decomposition of the sugar molecules into water and carbon. The external pressure times the original volume is a measure of the energy that is locally preserved (for a short period) for the activation of further reactions. In the absence of such external pressure, more energy is immediately converted into translational kinetic energy of the surroundings. This kinetic energy is not available for activating further molecules. While it will eventually be converted into heat, this does not happen until the energy has been distributed over much bigger volumes and thereby has become ineffective.

However, there are two strong reasons against this explanation. One is quantitative. The actual contribution of the external pressure to the available thermal energy in the explosion wave can be obtained from the theory of shock propagation. This energy per unit mass is $p\Delta V/2$, where p is the external pressure and ΔV is the change of the volume of 1g during the compression phase of the explosion. To this term further contributions must be added which are due to the fact that the final pressure and the volume change ΔV also depend on the external pressure. These terms can increase the contribution $p\Delta V/2$. Nevertheless,

this latter quantity is a better estimate of the additional internal energy than pV and $p\Delta V/2$ will probably not amount to much more than 10% of pV. This amount is too small to cause a substantial difference in the detonation process.

The second argument is of a qualitative nature. The effect of the external pressure on the energy fails to explain the apparent influence of shear stress.

Another explanation that has been proposed is connected with the considerable local heating which great shear stresses may produce. However, a detonation requires that appropriate energy storage should be available everywhere in the crystal. Strong local heating could explain only the triggering of the detonation wave and not the propagation of that wave. The real problem is to explain the mechanism of this propagation, and local production of heat is of no real help in this respect.

It is most probable that the explanation of the phenomenon is connected with a lowering of the activation energy. Another way of stating this is that the work stored in the material due to compression and shear becomes available for the production of an appropriate activated state which forms the lowest barrier between the original compound and the final products of decomposition.

It seems plausible that a lowering of a potential barrier by 0.5 to 1 ev could be sufficient to transform an exothermic reaction into an explosive process. Such amounts of energy are delivered by the work of compression

$$\int p dV$$

at 50,000 atm to a volume of approximately 100 cubic Angstroms. In sugar, such volumes are occupied by a section of the carbon chain containing three carbon atoms (the oxygen and hydrogen atoms attached to the carbon chain are of course included in this volume). It may seem a little difficult to imagine that all of this energy

should be made available to the correct degree of freedom which consists in the motion of the atoms from the original state into the activated position. The following model may illustrate one way in which this could happen.

Let us symbolically represent the motion of the system from the original state through the activated state into the final state by the motion of a point from a somewhat higher parabola to a somewhat lower parabola. This situation is shown in Fig. 1(a). Points 1, 2, and 3 correspond to the original position, the activated state, and the end product. If we assume that the crystal is compressed, it is natural to assume that the axes of the two parabolas will come closer to each other. Then a situation will arise as shown in Fig. 1(b). It will be noticed that the two parabolas are similar in the two figures and that the difference of their minimum energies is also similar. But the two parabolas will lie closer to each other, and therefore their point of intersection 2, which is the activated state, has been lowered to a considerable extent. Because the two curves intersect in a region where they are rising steeply, a relatively small displacement can produce a considerable lowering of the activation energy. It would seem quite possible that a displacement by 0.2 or 0.3 Angstroms could lower the point of intersection by 0.5 or 1.0 ev.

The question, of course, arises whether the same effect could have been achieved by a temperature excitation of the original substance. Such a temperature excitation could distort any portion of the original substance and thereby bring the old and the new equilibrium positions closer together. Since temperature distributes energy equally between degrees of freedom, any such temperature excitation requires an energy that must be as great as the increase of the activated state which we wish to accomplish.

In the compressed crystal, however, the activated state can depend on the position of all the neighboring atoms. That the position of a dozen atoms should have a strong influence on the height of an activated state is not too surprising. The volume of these atoms contains a large enough portion of the compression energy to account for the change in activation energy.

It should, of course, be realized that this model represents only one of several possibilities by which the probability of the activated state can be increased in an effective manner. In particular, it is possible that the entropy of the activated state will be increased by the compression.

In view of the experimental facts concerning shear stress, it is of particular interest to find out whether by shearing the substance one might accomplish a greater storage of energy and thereby make more energy available for the reduction of the activated state. As a rule, the shear stress is considerably smaller than the stress in the compression. On the other hand, the shear strain is very much greater than the displacement of the atoms in the compression. It is therefore quite possible that the work performed by the shear stresses make the greatest contribution to the energy store of the substance. It would be of interest to find methods by which to measure the energy that has been made available to the substance by the shear stresses. This could be done by measuring the work of the shear stresses and by subtracting from this work the energy that has been transformed into heat through local slippages. In an ideal experiment these local slippages should be avoided and the stress should not contribute to the heating of the crystal prior to the explosive transformation.

An additional interesting approach would be to investigate the dependence of the detonation temperature on the state of strain. If the activation energy depends linearly on the displacements under strain (as is the case in the model that we propose), then the temperature should be a linear function of the components of the strain. If, in addition, the activation entropy should depend linearly on the displacements, then the detonation temperature should be a ratio of two expressions that are linear in the strain components. It is entirely possible, however, that the activation energy is not linear in the displacements, but depends more directly on the compression work per unit volume or on a specific fraction of that work.

Experiments have not yet indicated a relation between the state of strain and the temperature of detonation.

LEGENDS

Fig. 1. Representation of the motion of the system from the original state (1) through the activated state (2) into the final state (3). (a) Without compression; (b) after compression.

REFERENCES

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[1] P. W. Bridgman, Phys. Rev. 48, 825 (1935).

[2] The author is indebted to David T. Griggs, George C. Kennedy, and Willard F. Libby for information concerning preliminary experimental results and stimulating discussions on the theoretical problem.

[3] John von Neumann, Office of Scientific Research and Development Report No. 549, 1942.

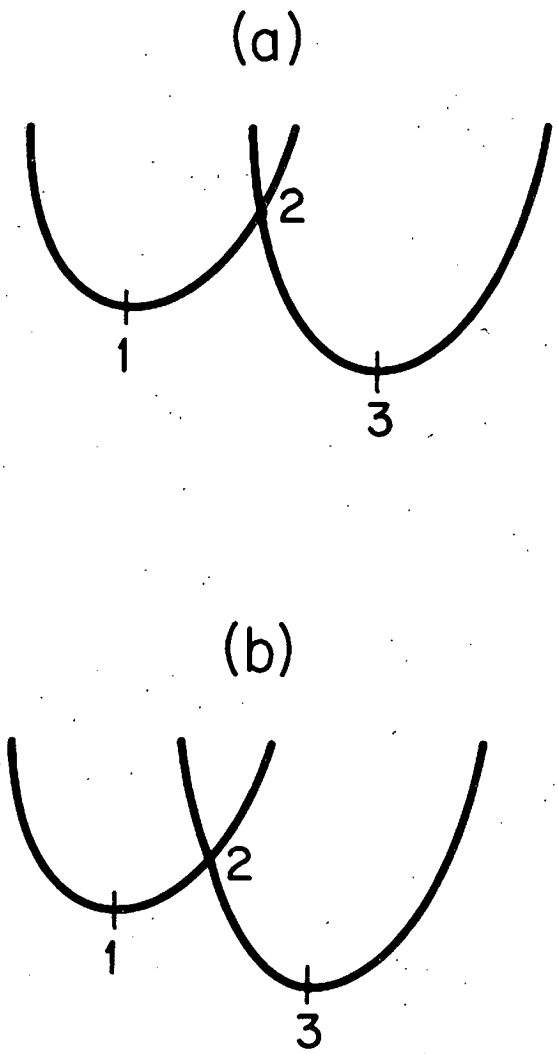

Fig. 1

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