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TI SHOCK COMPRESSION CHEMISTRY

IN MATERIALS SYNTHESIS AND PROCESSING

Report of the

$CR\,4$ Committee on Shock Compression Chemistry
in Materials Synthesis and Processing

$CR\,3$ National Materials Advisory Board
$CR\,2$ Commission on Engineering and Technical Systems
$OP\,1$ National Research Council

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ABSTRACT

Shock-wave chemistry deals with the chemical phenomena associated with dynamic compression of solids or liquids by either explosive or high-speed impact. Some of these phenomena are phase transformations, activation of powders, production of solid solutions of inorganic substances, synthesis of new compounds, polymerization and cross-linking of organic materials, and decomposition of complex substances into simpler ones. The field is thought to hold promise for future technological developments, but a number of scientific questions must be answered before that promise can be fulfilled. A National Research Council committee was charged with reviewing the present state of activities in this field, considering potential scientific and technological utilities, and recommending a course for future support of research. This report contains the committee's findings, conclusions, and recommendations. There are substantial grounds for believing that the novel physical and chemical processes involved may ultimately serve as the basis for useful technologies. Many of the questions that need to be answered, however, are not being addressed by work now in progress. The committee recommends that the present research program in the United States be expanded in an orderly manner; specific areas of emphasis are described.

PREFACE

Historically, chemistry has been a science of end states. Substances were mixed and processed, and the reaction products were collected and analyzed. The results were recorded, controllable parameters were changed, and the process was repeated. The technology of chemistry is still of this nature, but the science of chemistry has turned to questions of kinetics and processes on a microscopic scale. Shock chemistry, as it now exists, is an exercise in old-fashioned chemistry with an unfamiliar and poorly characterized process. It raises a host of scientific questions that cry out to be solved, and it holds promise for future technological developments. Evaluations of that promise and of the importance of these scientific questions are required. Because the process is unfamiliar, it challenges the science of modern chemistry to evaluate it and fit it into the theoretical structure so carefully built during the past 100 years. It challenges modern technology to find ways to use the novel phenomena associated with shock compression.

These are the two questions addressed here by the Committee on Shock Compression Chemistry in Materials Synthesis and Processing. To restate them:

o   On the basis of past accomplishments and present knowledge, is there justification for believing that continuing or intensified research in the field of shock chemistry will lead to processing methods or material modifications that are profitable in a broad sense? Are the processes that occur in shock chemistry straightforward applications of present chemical concepts, or do they represent unfamiliar processes which may require expansion of the theoretical framework of chemistry?

o   In the latter case, is there ground for believing that existing or promising techniques, either theoretical or experimental, provide the tools needed to address the questions, and will it be scientifically profitable to pursue them?

The committee's deliberations were aided immeasurably by Robert A. Graham and Brian W. Dodson of Sandia National Laboratories, whose Bibliography on Shock Induced Chemistry provided a wealth of information.

We are grateful to the Battelle Seminars and Studies Program Conference Center in Seattle for providing the facilities for a workshop which was held to obtain information for this report. Lorna Slominski, Battelle's coordinator for the meeting, provided tireless assistance in making it a success.

v

Finally, we wish to gratefully acknowledge the contributions of the participants in the Seattle workshop: Edwin K. Beauchamp, Anthony J. Campillo, William G. Dauben, Brian W. Dodson, John J. Gilman, Dennis E. Grady, Robert A. Graham, Yuki Horie, John C. Jamieson, Bruno Morosin, Malcolm F. Nicol, Hayne Palmour III, Roger S. Porter, Akira Sawaoka, Stephen C. Schmidt, Earl F. Skelton, and Eugene L. Venturini. Their presentations and presence for discussions added much timely information for the committee's use in this report.

The committee has not considered the problems of energetic materials directly; they are well considered elsewhere. There are close relations among problems considered here and those of detonation and combustion, and research workers must be aware of this. But bridges should be constructed individually, not collectively.

<div align="right">George E. Duvall</div>

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SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

"Shock wave chemistry" is the collective term used to describe a host of physicochemical phenomena associated with dynamic compression of solids or liquids by either explosive or high-speed impact. Peak pressures involved are large, ranging from 2 to 200 GPa. Phenomena include compaction of powders, phase transformations, activation of powders, production of solid solutions of inorganic substances, synthesis of new compounds, polymerization and cross-linking of organic materials, and decomposition of complex substances into simpler ones.

Work on these problems was started in the United States in the mid-1950s and dropped in the early 1960s, largely because of lack of support. Research has been pursued vigorously in the USSR since that time and has matured as a result of those efforts. By the standards of conventional chemistry, the subject is still regarded as being in an exploratory stage. Scientists in Japan have maintained an interest and are actively pursuing some aspects, of which dynamic compaction is the most visible. Renewed interest in the United States in the late 1970s resulted in efforts on a modest scale, principally at Sandia National Laboratories.

Interest has been motivated largely by the hope that further research will lead to new techniques for production of esoteric materials. This hope has been fulfilled in two cases—production of synthetic diamond and of cubic boron nitride—and there is considerable promise that new methods for producing better powder compacts will be forthcoming.

The novelty of some products has aroused considerable interest in the scientific aspects of shock compression. Questions that have been asked but are unanswered—or only partially answered—relate to problems of nonequilibrium temperatures, the dynamics of molecular deformation and excitation, the nucleation of defects, and the generation of electric fields, all in the shock front. There is also uncertainty about the relative influences of pressure and temperature behind the shock front. Much of the uncertainty and latent controversy is summed up by asking whether the shock effect is "benign" or "catastrophic." The former term implies that the observed effects are a consequence of high pressure,

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high temperature, and conventional quasi-static chemical kinetics. The latter term is used to indicate the belief that there are processes initiated in the shock front that are unique to shock excitation and may not be included in the normal lexicon of chemical processes. Microscopic molecular-state distributions induced during shock wave compression may be so far from equilibrium that the usual chemical kinetic calculations based on equilibrium distributions of states would be seriously in error. The weight of evidence leans toward the catastrophic concept, but the question is still open.

CONCLUSIONS

As a result of its deliberations, the committee finds that there are substantial grounds for believing that novel physical and chemical processes are involved in the compression and heating of materials by shock waves and that some of these processes may ultimately serve as the basis for useful technologies. Many questions, both technological and scientific, are left unanswered by the existing literature. Some of these are being addressed by work in progress, others are not.

In spite of its inactivity in shock wave chemistry, the United States is in a good position to mount an effective program in this field. Major shock wave physics groups are active at several Department of Energy and Department of Defense laboratories, contract research institutes, and at two universities. Some evidence of the high level of activity in this area is provided by the nearly 200 papers submitted for presentation at the 1983 American Physical Society Topical Conference on Shock Wave Physics (July 18–21, 1983, Sante Fe, New Mexico); more than 300 U.S. and 65 foreign scientists attended the conference.

The scarcity of scientists trained in shock compression methods and the restricted availability of facilities pose a limitation on an immediate, significant expansion in the field. Training in this field is time-consuming, so the situation could not be changed quickly.

Technologically interesting processes in the existing catalog of shock chemistry observations include the following:

o   Dynamic compaction and sintering, already addressed elsewhere [Committee on Dynamic Compaction of Metal and Ceramic Powders, 1983], particularly of substances like Si_3N_4, which do not sinter easily but have especially desirable properties;

o   Activation of catalysts, which are reported to be improved by as much as three orders of magnitude by shock treatment;

o   Production of unusual polymers or alteration of polymer properties.

The scientific and technical problems that stand in the way of implementing technology are challenging but appear to be surmountable. Some are particularly interesting, since their understanding may require extending modern chemical concepts and methods into relatively unexplored regions. For this reason the ultimate value of understanding may transcend the importance of immediate applications. These problems deal with energy partition and stability of large molecules, nonequilibrium excitations, and development of defect structures in solids.

RECOMMENDATIONS

1. The present shock wave research program in the United States should be continued and modestly expanded to include a greater emphasis on chemistry. The expansion should be conducted in an orderly manner. A sustained effort will be more effective than a crash program.

2. A concerted effort should be made to draw interested and competent persons into the program from a variety of scientific disciplines—e.g., materials sciences, chemistry, ceramics, polymers, and metallurgy.

3. An effort should be made to establish, maintain, and staff a shock wave research facility in such a way that the facility and trained personnel will be available to collaborating scientists for investigation of special problems.

4. A significant part of the effort should be committed to systematic study of model systems, including metals and conic crystals, using the best available techniques for determining and controlling shock parameters throughout the experiments. A similar effort is required for characterizing the reagents and their products and for controlling impurities.

5. The shock program should be supplemented by supporting static pressure and temperature measurements for the model systems, and by other supporting research as required.

6. Efforts to monitor the progress of reactions in the shock front and throughout the experiment should be continued and expanded. The development of new probes—for example, the recent promising application of advanced optical spectroscopies—is strongly encouraged.

7. Theoretical and numerical studies of the shock process as related to chemical reactions should be continued and encouraged.

8. The relative effects of single-shock loading, stepwise loading, and isentropic compression should be evaluated and examined for qualitative and quantitative differences.

9. Serious efforts should be made to measure temperature and shear stress in dynamic compression. The former has a marked effect on end products and is not well known. The latter may play an important role in shock-induced reactions.

10. Geometric scaling experiments should be undertaken to determine the extent to which rate-dependent processes are involved.

If all or any part of these recommendations are followed, support should be adequate and sufficiently prolonged to allow success or valid evaluation of the problems.

1. INTRODUCTION

During the past 30 years, experiments have been conducted in several nations on a variety of problems that have come to be lumped under the name of "shock wave chemistry." Some of the results that have been reported are in fields where technological innovations could be of considerable value.

This committee has been charged with reviewing the state of these activities, considering their potential utilities (both scientific and technological), and recommending a course of action for future federal support of such work.

In conducting its study the committee relied to a large extent on a limited-attendance workshop held to obtain views and information from a broad representation of the science and technology community. This has been supplemented by reference to the rather large body of existing literature, which can be consulted with the aid of a published bibliography [Graham and Dodson, 1980] and several recent review articles [Adadurov and Gol'danskii, 1981; Dodson and Graham, 1981; Morosin and Graham, 1981]. (References are collected at the end of this report.)

The remainder of this chapter is devoted to describing the shock process, the kinds of experiments used to study problems in shock chemistry, and some general remarks relating to such experiments. Chapters 2 through 5 of this report contain evaluations of the four areas into which shock wave chemistry falls: organic, inorganic, compaction and sintering of powders, and fundamental processes. Each of these chapters includes a brief review of the status of work, a discussion of the work, and recommendations relating to that area. The subject of powder compaction and sintering is treated only briefly because a comprehensive study on this subject has been recently published [Committee on Dynamic Compaction of Metal and Ceramic Powders, 1983].

THE SHOCK PROCESS

A shock wave is a nonlinear, usually large-amplitude disturbance, propagating at supersonic speed, across which the pressure, density, temperature, and related physical parameters change in a near-discontinuous manner. Although mathematical discontinuities do not occur in real materials, discontinuities are often used to approximate

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those disturbances having the very short rise times observed in experiments. Unlike acoustic waves, shock waves are characterized by amplitude dependent wave velocities.

Shock compression is an irreversible process accompanied by a temperature increase that exceeds that of equilibrium isentropic compression. For condensed matter the interatomic (or intermolecular) forces are strong, and large pressures are required for even modest compressions (a few percent). Accordingly, temperature changes are small compared to those produced by shocks in gases. Even so, at the very highest pressures (of the order of 10^7 atmosphere or 1000 GPa) reported in condensed materials, the compressions are large (approaching a factor of 2), and temperature changes are also large (of the order of 5×10^4 degrees Kelvin).

Scientific applications of shock wave techniques have included mechanical, thermodynamic, kinetic, electrical, optical, and chemical studies, with particular emphasis on the first of these. The scientific value of shock studies lies in these characteristics of shock waves:

o   Very large pressure can be produced--up to hundreds of gigapascals.

o   Application of pressure, and the mechanical and thermal parameters that accompany it, is very rapid; rise times may be of the order of picoseconds.

o   In well-designed planar experiments the macroscopic strain may be strictly uniaxial, and the distribution of state parameters in the sample volume can be made very uniform. Other geometries than plane are sometimes used; in these also the strain is known precisely, but it is no longer uniaxial.

These conditions enable the experimenter to observe material response under unusual and well-controlled conditions, thereby providing stringent tests of the understanding of fundamental physical processes.

Technological applications of shock waves are older even than explosives. Such applications are both military and commercial, and many of them are so familiar that we no longer see them. Some of the less familiar ones are explosive welding, explosive metal hardening, and explosive metal forming, which are used worldwide, and synthesis of diamond from graphite and of cubic boron nitride from the normal form. A new chapter in the subject was opened in 1961 with the discovery of the conversion of graphite to diamond in a shock process [DeCarli and Jamieson, 1961]. The history is reviewed in more detail in Chapter 3, but the result is that we are seeing a worldwide broadening of perspective and an accelerating interest in shock wave technology. The principal reason is that explosives are cheap, shock wave pressures are large, and it seems to be possible to economically produce at least a few products in competition with more conventional methods. Conditions in

the shock front itself are not well understood, and there is continuing speculation on the possibility that processes occurring during this rapid compression may either render void any comparison with static measurements or provide opportunities for new insights into material behavior, depending on one's basic point of view.

EXPERIMENTS

Shock experiments fall into two categories--recovery experiments and dynamic experiments. Recovery experiments are designed so that the sample to be studied is preserved after the shock wave and all consequent stresses have vanished from the sample and container. After the experiment the container is taken apart, and the sample is removed and subjected to various kinds of analyses to determine how it differs from the starting material.

In evaluation of experiments, it is important to recognize differences among the various kinds of dynamic loading used. Two kinds of geometry are used--cylindrical and plane (or plane-like). In the former the load is normally applied with an explosive encasing a cylindrical capsule containing the sample. It is relatively cheap and quick and thus is useful for rapid surveys of large numbers of materials. The stress/time history varies greatly throughout the sample volume. It is sensitive to dimensions of the system, and peak pressures vary with explosive and sample. "Pressure" refers in general to the pressure tensor, $P_{ij} = -\sigma_{ij}$, where σ is stress as usually used, being positive in tension. Stresses are so poorly known in most recovery experiments that "pressure" is used in a generic sense to denote a quantity of the order of trace$(-\sigma)/3$.

With plane geometry there is, at one extreme, the idealized plane wave experiment, in which the sample is subjected only to uniaxial strain and compression is accomplished by means of a single jump in pressure from initial to final compressed state. In dynamic experiments this ideal can be closely realized. In recovery experiments it is almost impossible to achieve, and various compromises are made.

Mechanical measurements of the passage of a single shock are relatively simple and can be made almost exactly plane and uniaxial with very thin sampling volumes. Dynamic optical and electrical measurements can be plane and uniaxial (although they often are not), but they may involve a sampling volume in which the material state varies throughout the volume. These are usually (but not necessarily) single-shock experiments.

Recovery experiments can be made to approximate the plane, uniaxial, single-shock condition by using "momentum traps" intended to protect the sample from all but the first passage of the shock wave and its following rarefaction [see Figure 1-1(a)]. Such experiments are difficult, tedious, and costly. The more common practice of enclosing the specimen in a thick, strong capsule leads to very complicated stress and
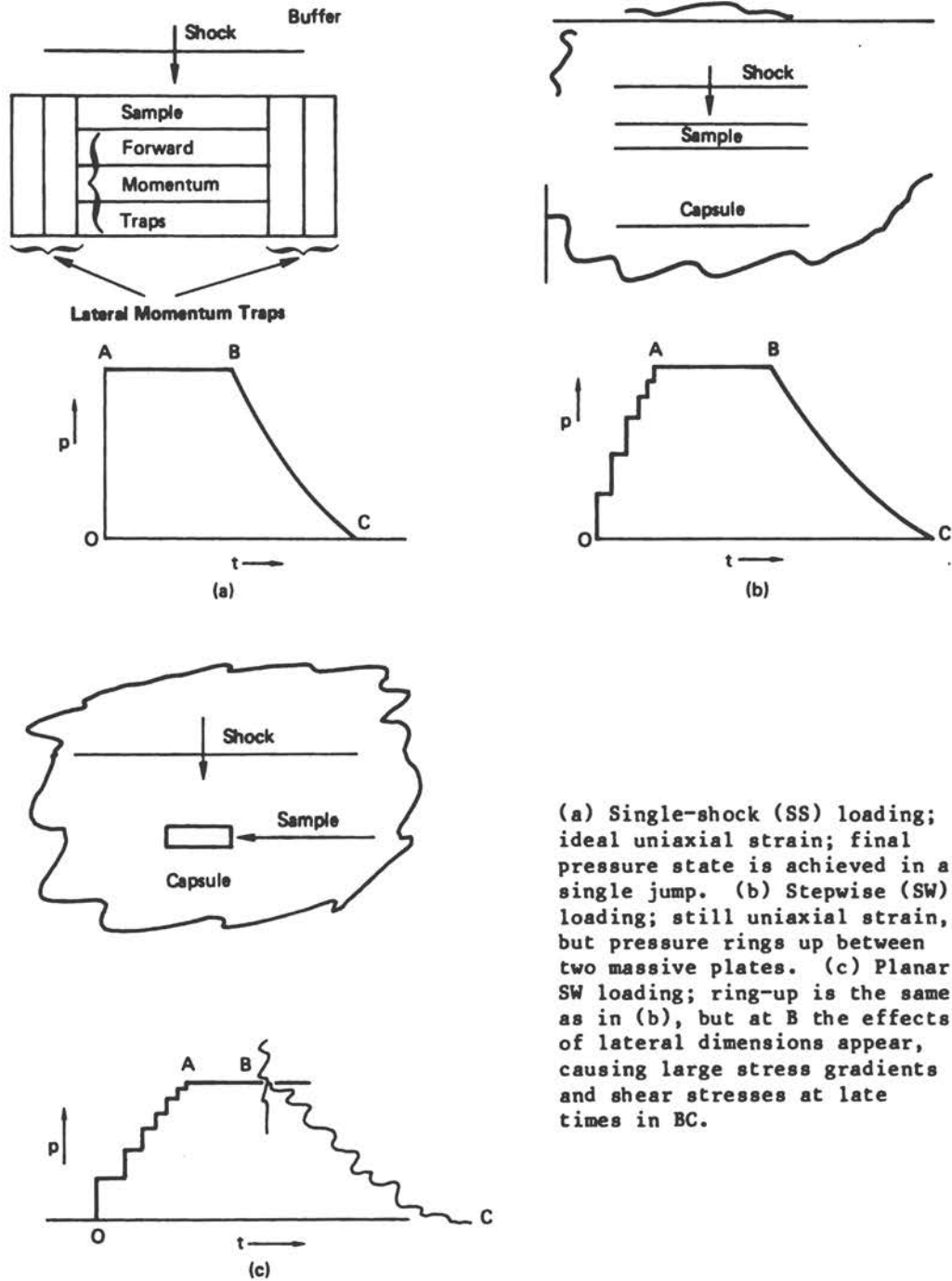
FIGURE 1-1.   Loading curves, p(t), for different experiments. Compression phase is OA; AB is "quiescent period" (i.e., uniform pressure state); BC is rarefaction (unloading) wave.

(a) Single-shock (SS) loading; ideal uniaxial strain; final pressure state is achieved in a single jump. (b) Stepwise (SW) loading; still uniaxial strain, but pressure rings up between two massive plates. (c) Planar SW loading; ring-up is the same as in (b), but at B the effects of lateral dimensions appear, causing large stress gradients and shear stresses at late times in BC.

temperature histories. In the most ideal situation, in which uniaxial strain is maintained in the capsule, maximum pressure and temperature are reached by means of a series of steps corresponding to reverbation of the shock in the sample between the two faces of the confining capsule [see Figure 1-1(b)].

The third case [Figure 1-1(c)] cannot be fully described in a single two-dimensional diagram. In real capsules the width of the specimen is finite, and lateral waves can significantly affect the stress history. Calculations for a specific case can be made using two-dimensional wave codes. An example is given by Davison, Webb, and Graham [1981].

In this report, loading of the type shown in Figure 1-1(a) will be called single shock (SS) loading, and loading of types (b) and (c) in Figure 1-1 will be called stepwise (SW) loading. A third type of plane dynamic loading, described by Adadurov and Gol'danskii [1981] has been called dynamic isentropic compression (DIC). In this the steps in SW loading are eliminated, and dP/dt at a point is continuous and small enough to minimize irreversible effects. (This is true in principle and very nearly true in practice for compact solids. It may be quite far from true in a powder sample.)

There are two important differences among these three kinds of loading. First is the temperature history. The temperature reached in SW loading to a given maximum pressure is less than the temperature reached in a single shock to the same pressure and greater than that reached in DIC loading. The exact value depends on material and loading details. For example, in liquid carbon disulfide at 6.0 GPa, the temperatures produced by SS, SW, and DIC loading are approximately 1240, 775, and 580 degrees Kelvin, respectively [Duvall, 1984].

Second, if there are indeed peculiar nonequilibrium physical and chemical processes associated with very large gradients in the shock front, they are probably greater for large jumps in pressure than for small, because gradients normally increase as magnitude of the shock jump increases. Such effects will then be greatest for SS loading, least for DIC, and intermediate for SW loading. This point does not appear to have been addressed clearly in past work; it is discussed further in Chapter 5.

Some of the points mentioned above are treated more fully in the literature [Adadurov, Gol'danskii, and Yampol'skii, 1973; Adadurov, Bavina, Breusov, Drobyshev, and Pershin, 1972; Dremin, Ivanov, and Mikhailov, 1973; and Jones and Stevens, 1972].

There are many designs for recovery experiments [Batsanov, 1982]. A planar experiment that provides SW loading and is intended to preserve a semblance of uniaxial strain in the sample is shown in Figure 1-2. In use, a plane wave is induced·in the explosive at the top of the sample. This produces a plane shock wave in the center of the steel beneath it, with rarefactions coming in from the sides; the steel produces some

EXPLOSIVE LOADING WITH SAMPLE RECOVERY
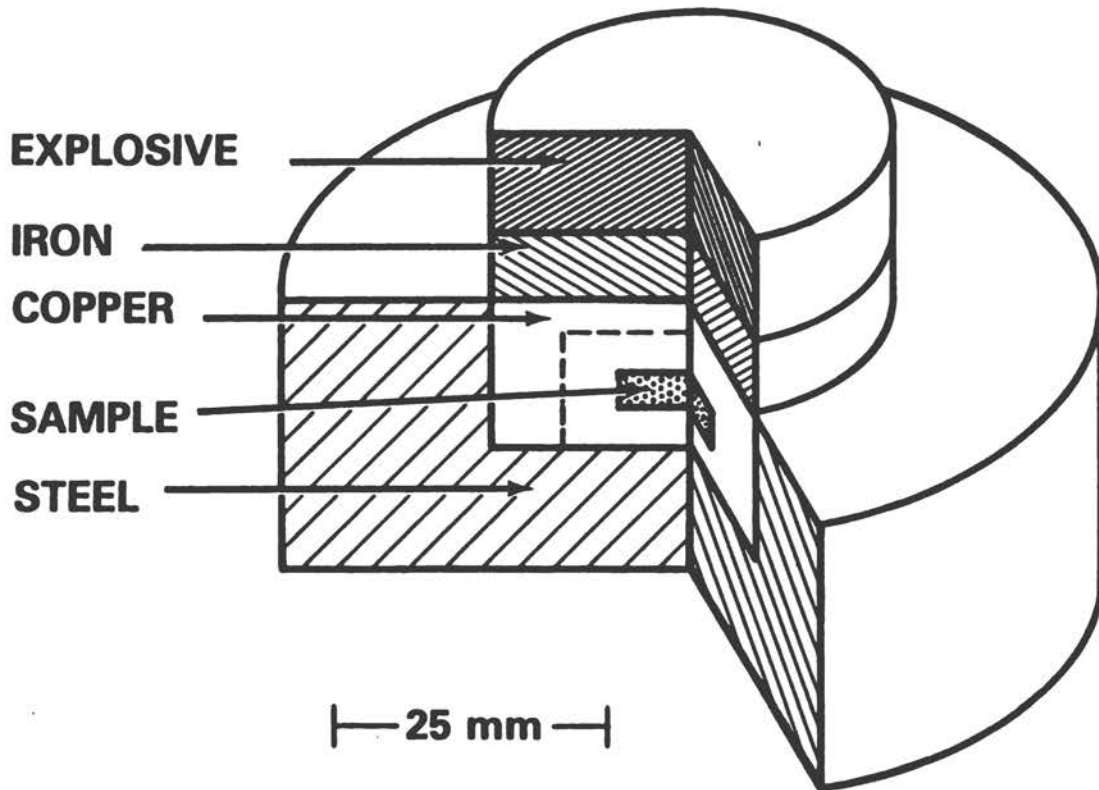
FIGURE 1-2. Cutaway view of experimental assembly for recovery experiment [from Davison, Webb, and Graham, 1981; used with permission].

shaping of the wave, making it more square than the wave in the explosive. This shaped wave passes into the copper capsule with little modification, hence into the sample. This provides SW loading modified by lateral rarefactions, as in Figure 1-1(c). There is also a focusing effect in this arrangement that produces a significantly larger peak pressure than would be calculated for uniaxial strain. The dominant loading in this geometry is radial [Graham and Webb, 1983].

There are also many kinds of dynamic experiments. Most have been concerned with mechanical properties, but there have also been measurements of electrical, optical, and thermal properties. A dynamic experiment that is germane to shock chemistry is measurement of absorption spectra of materials as they change from the shocked to the unshocked state. One such experiment is shown in Figure 1-3 [Duvall et al., 1982]. In this experiment, uniaxial strain is maintained in the sample for the duration of observation, but the loading is SW because the compressible liquid sample is contained in a penny-shaped cell, bounded front and back by transparent sapphire disks. Just before impact a xenon flash lamp is pulsed, producing a spectrally broad light that traverses the sample assembly, passes through a grating spectrograph, and is recorded on 35-mm film by means of a rotating mirror streak camera. The record on the film has wavelength varying across the film strip, time varying along the strip, and density varying with reflectivity or transmissivity of the sample. Some results of such experiments are shown by Ogilvie and Duvall [1983].
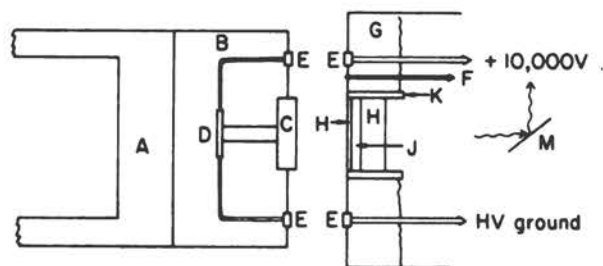
FIGURE 1-3.   Schematic representation of light transmission experiment. A, aluminum body of projectile; B, PMMA/epoxy projectile head; C, sapphire impactor; D, Xe flash lamp; E, high-voltage connectors; F, trigger pin for oscilloscopes; G, epoxy target body; H, sapphire plates of test cell; J, cavity containing liquid CS_2; K, brass container for test cell; M, mirror that reflects light into objective mirror of spectrograph [Duvall et al., 1982].

Pressure Control

Pressures achieved depend on geometry. In cylindrical geometry there is some advantage gained from convergence, and higher pressures can be achieved than in plane geometry. It is quite easy, for example, to generate a 500-GPa shock in tungsten in this way. The disadvantage is that gradients are very large and sample volume is small. The practical upper limit in plane geometry is about 200 GPa. Pressure relief is through the actions of rarefactions. When these interact, large tensions can be produced. Most of the fracture in shocked solids results from the interaction of rarefactions, augmented by shear stresses.

Temperature Control

The final temperature reached in the shock wave depends on mechanical and thermal properties of the sample. It also depends on the initial temperature of the sample. The reaction process can, in some cases, be significantly affected by quenching the assembly immediately after shocking, thereby reducing the extent of reactions produced by residual temperatures. For a given sample, the temperature depends in detail on the loading, as discussed earlier.

The temperature can be altered significantly by making the sample porous (if it is a solid). If the pores are filled with gas, the temperature can be made to approach 10^5 degrees Kelvin. If the gas is chemically active it may participate in the reaction, and hydrides of some metals have been produced in this way.

Time Control

For a given sample assembly the time of pressurization is controlled, first by the driver thickness and second by the geometry of the assembly. The quenching rarefaction may come from the rear of the driver, from lateral surfaces, or, in the case of plane waves, from the rear surface of the sample. For a practical laboratory experiment in plane geometry, the sample thickness is of the order of 10 percent of the assembly thickness or less, and the assembly diameter is of the order of 6 times the assembly thickness. For a 1-inch-diameter assembly the effective loading time is about a microsecond. For time-independent processes the dimensions scale as the time, so a 24-inch-diameter assembly, which would be quite large, would give a compression time of about 24 microseconds.

Calculations

It is not apparent from the existing literature, but it is nonetheless true that it is possible to characterize the stress-temperature-time profiles of complicated recovery fixtures using modern numerical wave codes. Good equations of state and constitutive relations are required. Given these and the necessary funds, the computations can be done very well indeed.

GLOBAL EFFORTS

The global distribution of effort in shock chemistry is dominated by work in the USSR. In a bibliography on the subject published in 1980 [Graham and Dodson, 1980], there are 116 citations of Soviet work, 2 of Japanese, and 1 from the United States. (In a 1983 update of this bibliography, the numbers are changed somewhat. The new bibliography is available on request [Graham, Morosin, and Dodson, 1983].) The work covered by the earlier bibliography is almost entirely recovery-related. The total record is not quite so out of balance as these numbers indicate. Japanese researchers have increased their activities significantly; they now have 8 high-pressure laboratories, each one doing both shock and static work, with work on powder compaction and sintering being particularly visible [Sawaoka, private communication]. The U.S. effort in recovery experiments has been almost nil until recently; there is now a substantial program under way at Sandia National Laboratories and smaller efforts at Los Alamos National Laboratories, Battelle Laboratories, and North Carolina State University.

If dynamic measurements are included, the situation is more balanced. The total U.S. effort in shock waves for the last 20 years has been almost entirely devoted to the dynamics of the shock process. Many of these dynamic measurements have important bearing on chemistry questions, but they do not replace recovery experiments.

This committee is in an unusual situation inasmuch as it is attempting to evaluate the importance of a field where almost all of the work has been done by persons relatively unknown to the western world, using techniques that are to some extent unfamiliar here. Publication standards in the USSR appear to differ from ours and published details of experimental procedures are sparse. The shock experimental process is violent by nature, controls are difficult to exercise, descriptions of starting materials and final products are incomplete, and the logic of cause and effect is noticeably different from that we know.

The first step in evaluation, then, must be establishment of the credibility of the Soviet experiments.

A few hard facts stand out. Synthetic diamonds have been and are being made by shock compression in the United States and in the USSR. Production is an important commercial activity in the United States. Cubic boron nitride has been made in the United States and is being made in Japan. Sawaoka in Japan has displayed impressive samples of sintered materials made by a combination of shock and conventional treatment [Sawaoka, 1983]. Wilkins [1983] of Lawrence Livermore National Laboratories has described a rational process producing metallic glasses. Morosin and colleagues at Sandia National Laboratories have found that simulations of Soviet experiments on polymerization have produced similar results in some cases [Morosin, 1983]. In collaboration

with Williams of the University of New Mexico, they have found preliminary indications of enhanced catalytic activity from shock-treated materials, in agreement with Soviet and Japanese results [Williams, 1983].

In an entirely different context, the worldwide geological community has independently cataloged many mineralogical changes that are peculiar to shock compression, and these are routinely used in the identification of meteorites and meteor craters [Boctor, Bell, and Mao, 1982].

Faced with a wealth of unusual data obtained from an ill-defined process--i.e., shock compression--Soviet workers have attempted to describe the process and its results rationally. One must conclude that there is at least a significant core of credibility in the Soviet work and that it is appropriate to take the stated experimental facts at face value, reserving final judgment until confirming work is done, as in all science. The shock process is divided into parts: the shock front, which passes over a molecule in 10^{-12} to 10^{-8} seconds, the approximately 10^{-6} second quasi-uniform pressure and temperature state behind the shock front,* the period of unloading or rarefaction, which may last several microseconds, and the long period of confinement at residual temperature and pressure before the capsule can be quenched. This is for SS loading. The additional complications of SW and nonplanar loading are obvious. With a small number of experiments, Soviet scientists have attempted to unravel the effects of these various stages of the shock process. Their conclusions, which must be regarded as tentative, can be roughly stated as follows:

1. The near-discontinuities in pressure associated with either SS or SW loading excite the reactants to a state or states in which the kinetics of reaction are accelerated. This excitation may be due to shear stresses in the shock front, to nonequilibrium energy distributions, to strong localized electric fields, or to other, as-yet unspecified phenomena.

2. Reactions proceed to something near completion in the quasi-uniform state behind the shock front. Temperature plays a key role in both kinetics and end states during this period. Some of the effects may be due to heterogeneities in temperature.

3. Rapid quenching of both pressure and temperature during the unloading phase helps to preserve the newly formed products.

As key elements in these processes the Soviet experimenters point to large concentrations of defects formed as a consequence of shear forces inherent in uniaxial compression and possibly influenced by pressure

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*Variations in pressure and temperature during this phase of the loading will be mainly due to chemical reactions. In extreme cases the variations may be very large.

gradients; to evidence of "super diffusion" of different molecular species; and to fracture phenomena. In solids, and particularly powders, the role of fracture is certainly important in the light of recent work on the electrical phenomena associated with fracture [Dickinson, Jensen, and Jahan-Latibari, 1984]. A survey of electrical measurements in shock-compressed material is given by Mineev and Ivanov [1976].

Somewhere in the process of evaluating shock chemical effects the terms "benign" and "catastrophic" have appeared to identify two extreme views of shock compression [Graham, 1981]. The former describes the process as being controlled by pressure (P) and temperature (T) with ordinary chemical kinetics; the latter as being controlled by P and T plus extraordinary events in the shock front, plus chemical kinetics. The Soviets have come down heavily on the side of "catastrophic," and an important part of future work will be to sharpen this concept and resolve the issues implied by the two terms.

EXPANDED PROGRAM REQUIREMENTS

Stable and Long-Range Support

Good results in shock wave research do not come quickly. Experiments are difficult and expensive. As an example, the Soviet work on polymerization of acrylamide has been carried out over a period of 15 years, and it cannot, in any sense, be considered complete. (It is described in some detail in Chapter 2.)

Thorough investigation of a substance requires, first of all, equations of state for starting materials and final products. These require Hugoniot (shock adiabat) measurements, specific heat and thermal expansivity, and careful theoretical considerations. Next in order is careful experimental design for single-shock, stepwise-shock, and dynamic isentropic loading. Computer calculations should be used extensively to ensure as full knowledge of the stress and temperature history of the sample as possible. The Soviet work is deficient in these matters.

Basic Problem

There are as yet no satisfactory methods for measuring temperature and shear stresses in shock waves. Both are important to shock chemistry, and both should be addressed in a comprehensive program, which would include a study of the suitability of the temperature concept in regions of rapid change.

Support Programs

Shock wave work should be adequately supported by static high-pressure studies. These form a reference base for evaluation of shock experiments and provide opportunity for independent control of temperature, pressure, and time.

Theoretical support is required, particularly in the areas of quantum chemistry and calculations of energy surfaces for deformed molecules and of molecular dynamics.

Personnel and Facilities

The number of scientists who are experienced in the methods of shock wave physics is sharply limited. Shock wave chemists are almost nonexistent. Participation of good scientists outside the shock wave community should be encouraged. This is perhaps best done by providing opportunities for collaboration and facilities where outsiders can work on research appointments for extended periods or where they may, under suitable circumstances, have experiments done with proper consideration for shock wave problems. Another method for aiding collaboration would be to promote participation in general American Physical Society and American Chemical Society meetings.

2. ORGANIC CHEMISTRY

STATUS

A large number of reactions have been cataloged as a result of recovery and analysis of products. In these experiments the chemical nature of the product can be determined, and this information produces speculation about the chemical processes involved. Loading conditions in recovery experiments are not well known, but they can be varied in useful, controlled ways [Adadurov and Gol'danskii, 1981; Adadurov, Gustov, and Yampol'skii, 1971]. Parameters commonly varied are pressure, initial temperature, loading time, and type of loading. Reactions studied include structural modifications, cross-linking of polymers, dissociation, isomerization, pyrolysis, and polymerization.

Dynamic measurements are not yet reaction specific. A cusp, or a region of negative curvature, in the pressure-volume Hugoniot usually denotes a rapid decrease of the shear stresses or a transition to a higher density state. There is normally no difficulty in separating these effects. Rapid increases in electrical conductivity may indicate high diffusion rates for ions or the mobilization of electrons by any of several mechanisms. Onset of opacity may result from shifts in absorption bands of existing molecules, creation of new complexes with absorption in the visible, or extinction caused by scattering or the onset of conduction [Ogilvie and Duvall, 1983]. Electrical polarization signals have been attributed to rotation of permanent dipoles by passage of the shock front or to creation of dipoles through the formation of defects or the scission of chemical bonds [Hauver, 1970; Styris and Duvall, 1970; Dick and Styris, 1975; Mineev and Ivanov, 1976; Duvall and Graham, 1977; and Graham, 1979].

Dynamic measurements of this kind will not resolve the problems of shock chemistry, for which purpose more specific, carefully pointed experiments are needed. They do provide important support for the speculations engendered by the results of recovery experiments. They may suggest new candidates for recovery studies. It is to be hoped that, in the future, emerging techniques for optical and vibrational spectroscopy may ultimately provide in situ evidence required to finally understand what happens as a result of the shock compression process [Campillo, 1983].

Dynamic Experiments

Table 2-1 contains information on compression, electrical conductivity, and optical properties of several organic materials studied in shock compression. If a cusp exists in the Hugoniot, the pressure at which it occurs is given. Most of the cusps given in the table occur at 10 GPa, more or less. Some occur at 20 GPa or more. There is some evidence that the high pressure values represent extensive decomposition and the lower values result from less drastic processes [Yakusheva, Yakushev, and Dremin, 1977; Ree, 1979].

Considerable theoretical attention has been given to the high-pressure, very high-temperature states of hydrocarbons by Ree [1979] and by Pucci and March [1981]. The former has proposed that hydrocarbons shocked to greater than approximately 10 GPa dissociate into carbon in the diamond phase and hydrogen in a condensed molecular phase. More recent calculations have shown that a distribution of light (C^1 - C^2) pyrolysis fragments provides an equally acceptable explanation of the methane Hugoniot. This proposal is supported by extensive computations and impressive correlations of theoretical and experimental curves [Nellis et al., to be published 1984]. An alternative model proposed by Pucci and March is based on the hypothesis that the C-H bonds are not broken, but there is a π electron transition that allows the π electrons to participate in intermolecular bonding. This leads to an alternative interpretation in which the cusp on the Hugoniot represents a transition from an isotropic liquid phase to a nematic liquid crystal phase [Pucci and March, 1981]. The question of what really happens at these pressures is still open.

Good electrical conductivity measurements are difficult to make during the passage of a shock wave through the sample, but the changes induced by shock are often so large that even very rough measurements yield useful information. David and Hamann [1960] reported measurements on water, methanol, acetic acid, propionic acid, 1/1-water/ethanol, ethanol acetone, and glycerol. The first five of these become very conductive at the approximate pressures given in Table 2-1 with σ approximately 1/(ohm cm). The other three do not. The results were attributed to self-ionization of the liquids, and a correlation between shock conductivity and magnitude of the autoprotolysis constant is described. A double shock experiment on water suggests that the temperature contribution to conductivity under shock is major.

Other electrical measurements include changes in the dielectric constant and shock-induced polarization. The former are normally rather small, but polarization currents can be quite substantial. Graham [1979] has examined polarization data for polymers and has shown that a positive correlation exists between magnitude of the polarization signal and complexity of the structural unit from which the polymer is made. He attributes the polarization signal to defect dipoles created by bond scission in the shock front and suggests that scission is easier for more

TABLE 2-1. Pressures (kilobars) at Which Anomalous Behavior Occurs Under Shock Compression for Various Organic Substances (Dynamic Experiments)

	RH Cusp	Opacity Onset	Electrical Conductivity	References
Acrylabmide	70			Veretnikov, Dremin, and Mikhailov, 1966
Polyacrylamide	70			Veretnikov, Dremin, and Mikhailov, 1966
Acrylonitrile[+]	43	43	43	Yakushev, Nabatov, and Yakusheva, 1974
Anthracene	180			Ree, 1979
Benzene	133,240	200		Dick, 1970
CCl$_4$	165	110	70	Dick, 1970; Yakushev, Nabatov, and Yakusheva, 1974; Walsh and Rice, 1957; Mitchell and Keeler, 1968
CS$_2$	48-62	∿70	70	Dick, 1970; Sheffield, 1978
Paraffin			∿65	Adadurov, Dremin, and Mikhailov, 1967
Phenthrene	400			Ree, 1979
Pyrene	250			Ree, 1979
Styrene*	60	60-70		Yakushev, Nabatov, and Yakusheva, 1974
Polystyrene	200			Los Alamos Scientific Laboratories, 1979
Trioxane			∿50	Adadurov, Dremin, and Mikhailov, 1967
Liquid CH$_4$	230			Nellis, Ree, Van Thiel, and Mitchell, 1981; Ross and Ree, 1980
Methanol			150	David and Hamann, 1960
Acetic acid			175	David and Hamann, 1960
Propionic acid			160	David and Hamann, 1960
1/1 water/ethanol			170	David and Hamann, 1960
Water**			100	Hamann and Linton, 1966

Note: 1 kb = 10 GPa.

[+]Authors propose pyrolysis as the density-increasing mechanism.
*The high-density phase of styrene is 10 percent more dense than polystyrene at the same shock pressure.
**Water is included because of its common use as a solvent.

complicated structures. This model is further supported by results from mechanochemistry, by the identification of free radicals in polymethylmethacrylate shocked to modest pressures, and by the existence of positive correlation between polarization signal and shock-induced conductivity [Graham, Richards, and Shrouf, 1980].

Loss of optical transmission in shocked liquids was first reported by Walsh and Rice [1957] for carbon tetrachloride and attributed to freezing. Color changes in explosively shocked polyvinylidine chloride were reported by Plauson and Mallory [1964] and attributed to chemical decompositions. Yakusheva, Yakushev, and Dremin [1971] used color photography to record the effects of shock waves on light transmitted through shocked liquids. They reported that benzene, carbon tetrachloride, acetone, dichlorethane, and nitromethane all appeared yellow after an 8- to 13-GPa shock entered the sample. Acetone, dichlorethane, and nitromethane subsequently became opaque. Introduction of a rarefaction immediately following the shock showed that for these pressures the shift in absorption was not reversible, but the pressure-dependence of this observation was not investigated. An absorption spectrogram of benzene at approximately 13 GPa showed that the absorption edge shifted to about 5500 Å when the shock entered the sample and remained there until the experiment ended. They attributed this shift to scattering from free carbon and proposed that the shock-induced reaction in unsaturated hydrocarbons is pyrolysis with the release of free carbon [Yakusheva, Yakushev, and Dremin, 1977].

Recent time-resolved electronic spectroscopy in liquid CS_2 has indicated that the shock-induced red shift of the red edge of the 3400-Å absorption band is proportional to pressure, in a cell of the kind shown in Figure 1-3, to approximately 8 GPa [Ogilvie and Duvall, 1983]. The shift is very large, but no satisfactory explanation has appeared. Direct measurements of the symmetric stretching mode in benzene have recently been made using stimulated Raman backscattering [Schmidt, Moore, Schiferl, and Shaner, 1983] and coherent anti-Stokes Raman scattering (CARS) [Schmidt, Moore, and Shaner, 1983]; the frequency shift is linear with pressure to 1.5 GPa and agrees with that measured statically. A CARS experiment in a benzene-deuterated benzene mixture showed no indication of deuterium exchange during the 1-microsecond duration of the experiment [Moore, Schmidt, and Shaner, 1983].

Recovery Experiments

Recovery experiments have been carried out in variations of the geometry shown in Figure 1-2 and, more often, in cylindrical geometry. Measurements of a large number of properties for a large variety of materials have been reported, and only a sample is presented here. The intent is to provide a suggestion of the state of research and the kinds of results that have been found.

The shocking of polymers may cause structural modifications at the molecular level on a large scale. Molecular modifications include cross-linking, diminution of molecular weight, or formation of three-dimensional networks; all of these are found in unsaturated elastomers like butadiene-nitrile, butadiene-styrene, and natural rubber [Adadurov, Gol'danskii, and Yampol'skii, 1973; Barkalov et al., 1966; Yampol'skii et al., 1968]. Natural rubber shocked to less than 15 GPa experiences only a decrease in molecular weight; three-dimensional networks appear above 15 GPa. Saturated elastomers show a decrease in molecular weight with little evidence of three-dimensional networks. Polymers with saturated bonds that have been studied include polymethylmethacrylate (PMMA), polypropylene (PP), polyethylene (PE), and polystyrene (PS). Cross-linking occurs in PS at 12 GPa; no observable molecular change has occurred in PP at 50 GPa, nor does it melt. At sufficiently large pressures dissociation and pyrolysis occur [Kargin et al., 1968; Kargin et al., 1971].
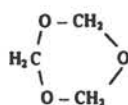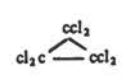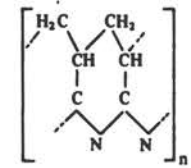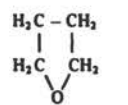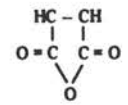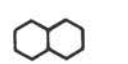
Shocking of PP to 20 GPa does change its microstructure. Starting from the crystalline form, it is converted to an apparently amorphous matrix containing small spheroidal crystallites. This final form is relatively independent of variations in the initial structure. When oriented films of PP are shocked to 20 GPa, their fibrous structure is replaced by the same kind of spherulite-in-matrix structure. Moreover, the dimensions of the film are unchanged. On heating to near the melting temperature, the film remained dimensionally stable, in contrast to unshocked samples. This same behavior has been observed in oriented fibers of polyester and plastic polyethylpiperazine. The microstructure of atactic polybutadiene rubber, an amorphorous polymer, changes from its normal striated form to a granular form when shocked to 10 GPa. Grain dimensions are approximately 1000 Å. Addition of phenylnaphthamine produces larger, better defined domains that are similar to the spherulites observed in polypropylene [Adadurov, Gol'danskii, and Yampol'skii, 1973; Kargin et al., 1971; Kargin et al., 1968].

The cross-linking in PS produced by shock pressures greater than 12 GPa has been compared with that produced by irradiation with gamma rays. The concentration of lateral bonds produced by shock waves is of the order of 100 times greater than that produced by gamma radiation for the same deposited energy [Adadurov, Gol'danskii, and Yampol'skii, 1973].

When small organic molecules in the condensed phase are shocked, polymers may be formed. Polymerization has been the most studied of organic reactions. Some of the polymers produced by shock are listed in Table 2-2, taken from the work by Babare, Dremin, Pershin, and Yakovlev, [1970]. Extreme examples insofar as pressure and yield are concerned are acrylamide, shown in the table, with a threshold shock pressure of 2 GPa and maximum yield of 60 percent at 11 GPa, and benzene, with a yield of 1.4 percent at 22.5 GPa. Elsewhere it was found that aliphatic compounds

TABLE 2-2. Polymers Formed in Shock Exposure

Examples of Polymerization of Liquid and Crystalline Monomers under Shock Compression Conditions

Monomer	Formula	Structure of polymer	Pressure range (kbar)	Yield (percent)	$\overline{M}v \times 10^{-3}$
		Crystalline monomers			
Acrylamide	$H_2C = CH - C \diagup^{O}_{\diagdown NH_2}$	$\left[\begin{array}{c} -CH_2 - CH -- \\ \mid \\ O = C - NH_2 \end{array} \right]_n$	20-80	6-60	30-500
Trioxane	$\begin{array}{c} O - CH_2 \\ H_2C \qquad O \\ O - CH_2 \end{array}$	$[-- CH_2 - O --]_{3n}$	30-110	2-16	130-1250
Hexachloro-cyclopropane	$cl_2c \overset{ccl_2}{\diagup\diagdown} ccl_2$	$\left[\begin{array}{ccc} cl & cl & cl \\ \mid & \mid & \mid \\ --C & -C & -C-- \\ \mid & \mid & \mid \\ cl & cl & cl \end{array} \right]_n$	130-230* (in copper)	30-50	-
		Liquid monomers			
Acrylo-nitrile	$H_2C = CH - C = N$	$\left[\begin{array}{cc} H_2C & CH_2 \\ CH & CH \\ C & C \\ N & N \end{array} \right]_n$	30-86* (in copper)	1.5-12	15-70
Styrene	$\begin{array}{c} H_2C = CH \\ \mid \\ C_8H_5 \end{array}$	$\left[\begin{array}{c} -- H_2C - CH -- \\ \mid \\ C_8H_5 \end{array} \right]_n$	88-167* (in copper)	3-17	8.8-90
Tetrahydro-furan	$\begin{array}{c} H_2C - CH_2 \\ \mid \qquad \mid \\ H_2C \quad CH_2 \\ O \end{array}$	$[- CH = CH - CH = CH - O -]_n$	108-220* (in steel)	0.3-2	2.8-17

The following materials are normally hard to polymerize:

Monomer	Formula	Structure of polymer	Pressure range (kbar)	Yield (percent)	$\overline{M}v \times 10^{-3}$
		Crystalline monomers			
Maleic anhydride	$\begin{array}{c} HC - CH \\ \mid \qquad \mid \\ O = C \quad C = O \\ O \end{array}$	$\left[\begin{array}{c} - HC - CH - \\ \mid \qquad \mid \\ O - C \quad C = O \\ O \end{array} \right]_n$	80-100* (in steel)	2.7-4	1.62
Naphthalene	⬡⬡	$\left[\begin{array}{c} - H_2C - CH_2 \quad CH = CH - \\ \end{array} \right]_n$	108-225* (in steel)	0.5-2.4	0.28-0.5
		Liquid monomers			
Benzene	⬡	$[- HC = CH -]_{3n}$	108-225* (in steel)	0.1-1.4	0.27-0.4
Benzalde-hyde	$\begin{array}{c} HC = O \\ \mid \\ C_8H_5 \end{array}$	$\left[\begin{array}{c} -- HC - O -- \\ \mid \\ C_8H_5 \end{array} \right]_n$	42-162* (in steel)	2.7-10	-
Butyro-nitrile	$C_3H_7 - C = N$	$\left[\begin{array}{c} -- C = N -- \\ \mid \\ C_3H_7 \end{array} \right]_n$	42-225* (in steel)	1.7-4.2	-
Tetrachloro-ethylene	$cl_2c = ccl_2$	$[- cl_2c - ccl_2 -]_n$	108-238* (in copper)	1.1-6	-

*The pressures were measured in the covers of the storage ampoules.

showed no evidence of polymerization when exposed to the same conditions of shock compression that produced polymers in benzene and naphthalene [Dremin and Babare, 1981; Dremin and Breusov, 1971]. Hexane, cyclohexane, and paraffin oil were practically unchanged, but the strained ring of hexachlorocyclopropane was 80 percent destroyed. Most of the polymers formed by shock can be produced by radical and ionic mechanisms, though some, shown in the lower part of the table, are hard to produce by means other than shock.

The entries in Table 2-2 all represent Soviet work. In the United States, Nathans and Holzer [1961] reported cracking and polymerization of hydrocarbons exposed to the effects of an underground nuclear explosion. Owens and Sharma [1980] have exposed samples of various explosives to single-shock waves with amplitudes below the initiation thresholds and compared the results with thermally decomposed samples and with UV-induced decomposition. Analysis of the products was by EPR measurements and X-ray photoelectron spectroscopy. Both shock- and UV-damaged TATB and RDX showed evidence of breaking of the C-N bonds between the benzene ring and the NO_2 groups. In TNT there is evidence for shock induced change in the bonding of CH or CH_3 with the adjacent oxygen of $-NO_2$.

Dodson [1981] has reported recovery work at Sandia Laboratories on acrylamide, adamantane, hexamethylenetetramine (HMT), naphthalene, and 1-6-diphenyl-2,4,-hexadiyne (DHD). His work with acrylamide partially confirms the results of Table 2-2, although it suggests that time and pressure are important variables. Adamantane and HMT are structural analogs with a significant difference: The barrier against molecular rotation is 3 kcal/mol in adamantane and 19 kcal/mol in HMT. The former responded to shock treatment with little or no change; the HMT produced several percent of a product that was insoluble in "normal organic reagents." Samples of naphthalene reacted violently to shock, bursting the capsule and leaving no residue for analysis. A DHD sample was recovered in a "totally degraded" state, being carbonized and "greatly reduced in weight." SW loading to 13 or 20 GPa was used in all of Dodson's experiments.

A listing or recital of reactions reported does not entirely convey the investigative process in depth. In an attempt to do this, the remainder of this chapter is devoted to a description of one substance, acrylamide, which has been discussed in many papers over a 15-year period. A second example, acrylonitrile, is the subject of an impressive paper by Yakushev, Nabatov, and Yakusheva [1974]. The following material is a summary of work on the polymerization of acrylamide given by Graham in 1981. It is taken directly from that reference [Dodson and Graham, 1981].

Reactivity of Acrylamide Under Shock Loading

Polymerization

Acrylamide has been polymerized under multiple compression shocking. These experiments involve the explosive loading of a polycrystalline acrylamide sample with dimensions of about 15 mm diameter and 1 mm thickness in steel [Ignatovich et al., 1970] or copper [Dodson, 1981] capsules. The sample thus reaches the input pressure in the capsule through multiple reverberations of the shock wave. When shocked as described, polymerization begins at a threshold pressure of about 2 GPa, following the reaction mechanism

$$
n\left[H_2C = CH - C \begin{smallmatrix} \nearrow O \\ \searrow NH_2 \end{smallmatrix} \right] \xrightarrow{\text{shock}} \left[\begin{smallmatrix} - H_2C - CH - \\ | \\ NH_2 \diagup C \diagdown O \end{smallmatrix} \right]_n
$$
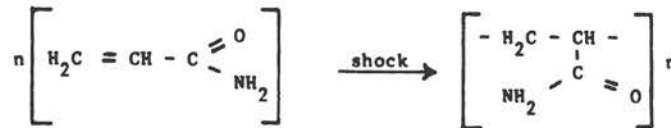
This polymer, a linear polyacrylamide, is water soluble.

At about 6 GPa, cross-linking of the polymer begins, probably through an imidization reaction, resulting in an insoluble product and evolution of ammonia (NH_3). A density transition corresponding to a 30 percent reduction in volume occurs between 9 and 11 GPa [Veretennikov, Dremin, and Mikhailov, 1966; Dulin et al., 1973] (see Figure 2-1). Above 18 GPa, the shocked acrylamide begins to degrade and carbonize.

Acrylamide polymerizes readily in conventional processes. It is therefore important to establish whether the polymerization is actually due to the catastrophic shock conditions or to some more benign effect of shock loading such as residual temperature. Such questions have been considered in some detail. The presence of a radical inhibitor, hydroquinone, is observed to have no effect on the shock-induced polymerization reaction [Babare, Dremin, and Mikhailov, 1969]. It was suggested that, if polymerization were caused by melting of the acrylamide, the inhibitor would prevent any reaction. When cooled to 77 degrees Kelvin and shocked, acrylamide still shows significant polymerization at 3 GPa, although the residual temperature is still well below room temperature [Adadurov, Gustov, and Yampol'skii, 1971]. By contrast, a slowly pulsed pressure of 5-7 GPa applied for milliseconds at room temperature produces no polymer [Yampol'skii and Ignatovich, 1970]. Enikolopyan [1979] has studied polymerization under static pressure in over 100 monomers, including acrylamide, and found that a pressure of 10 GPa is not sufficient to induce polymerization. It was concluded that the polymerization is not due simply to the benign application of temperature and pressure.
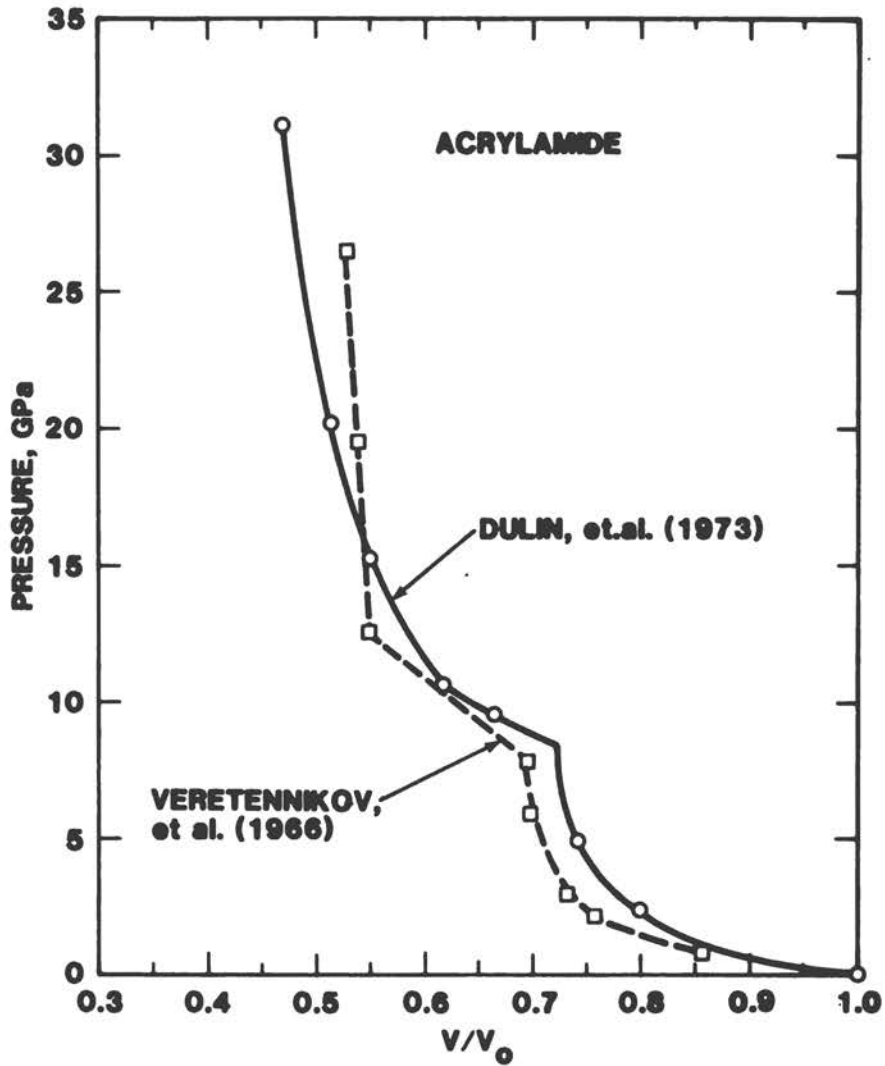
FIGURE 2-1. Pressure-volume relation for shocked acrylamide
[Veretennikov, Dremin, and Mikhailov, 1966; Dulin,
Zubarev, Shuikin, and Yampol'skii, 1973]. Acrylamide
has a 30 percent volume reduction between 9 and
11 GPa, which is correlated with a change in chemical
reactivity.

Reactivity in the Shock Front

The relevant data on acrylamide reactivity is summarized in Figures 2-2 and 2-3. Figure 2-2 shows polymer yield vs. molecular weight for single- and multiple-shock compression. Figures 2-3(a) and 2-3(b) show linear polyacrylamide molecular weight and polyacrylamide chain density, respectively, vs. shock pressure for multiple-compression shock loading of acrylamide. The polymer chain density, M, is defined as the number of polymer chains per initial monomer unit. It is important to note that M is about 3×10^{-6} for all single-compression experiments and for a 4-GPa multiple-compression experiment, even though molecular weights and polymer yields are strongly dependent on the loading details.

If we assume a radical mechanism with simple termination processes (either through combination, $R_{\dot{m}} + R_{\dot{n}} \rightarrow P_{m+n}$, or disproportionation, $R_{\dot{m}} + R_{\dot{n}} \rightarrow P_m + P_n$), the polymeric chain density corresponds to a radical density of about 3×10^6/cc. Similar radical densities have been found in shock-loaded polymers [Graham, Richards, and Shrouf, 1980]. The slow increase in M with pressure below 9 GPa for the multiple-compression work [Figure 2-3(b)] is probably due to reflected waves becoming strong enough to produce more free radicals.

The density transition near 9 GPa is strongly correlated with a large decrease in mean molecular weight of the polyacrylamide and a large increase in the polymer chain density. Both these changes are nearly two orders of magnitude. This indicates a major change in the polymerization mechanism associated with the density transition.

There are at least two possible mechanisms for the observed effects. One mechanism is that an additional species of radical is formed at a threshold pressure of about 9 GPa, thus increasing M and making simple termination reactions more likely, with a resulting decrease in molecular weight. However, the chemical makeup of the products does not change at this pressure, which is inconsistent with formation of a new radical species.

The other mechanism involves the activation of a new form of termination reaction: a transfer reaction. In this case, inactive polymer is formed by transferring the radical to a monomer unit, i.e., $R_{\dot{m}} + M \rightarrow P_m + R_1$. If such a termination reaction dominates, the much higher density of monomer compared to radicals will produce a higher density of shorter polymer chains; this is just the observed behavior. We therefore suggest that a chemical process is taking place in the shock front that activates the transfer termination mechanism. The observations above are not so much intended to identify a specific mechanism as to show that by combining chemical analysis with conventional shock compression data one can consider such questions in quantitative detail. [End of material from Dodson and Graham, 1981.]
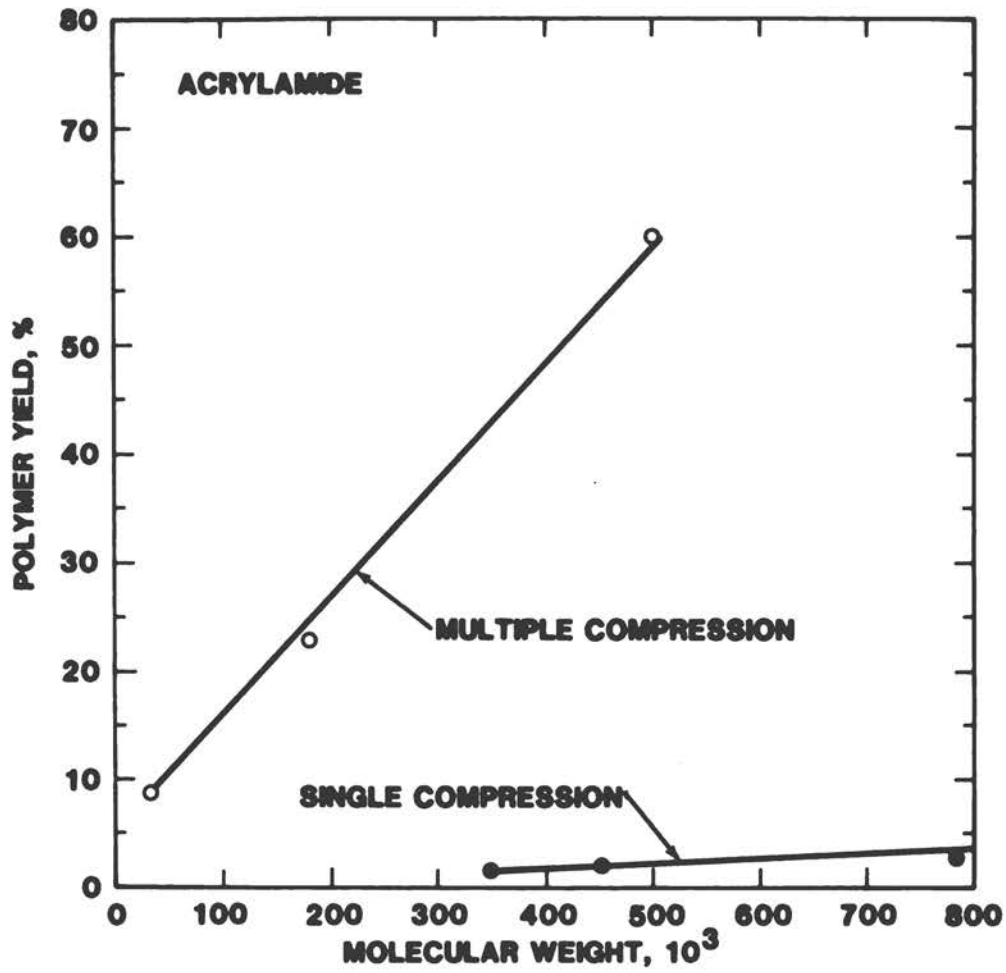
FIGURE 2-2.   Total polyacrylamide yield vs. linear polyacrylamide
molecular weight for single- and multiple-shock
loadings, based on data from Ignatovich et al. [1970].
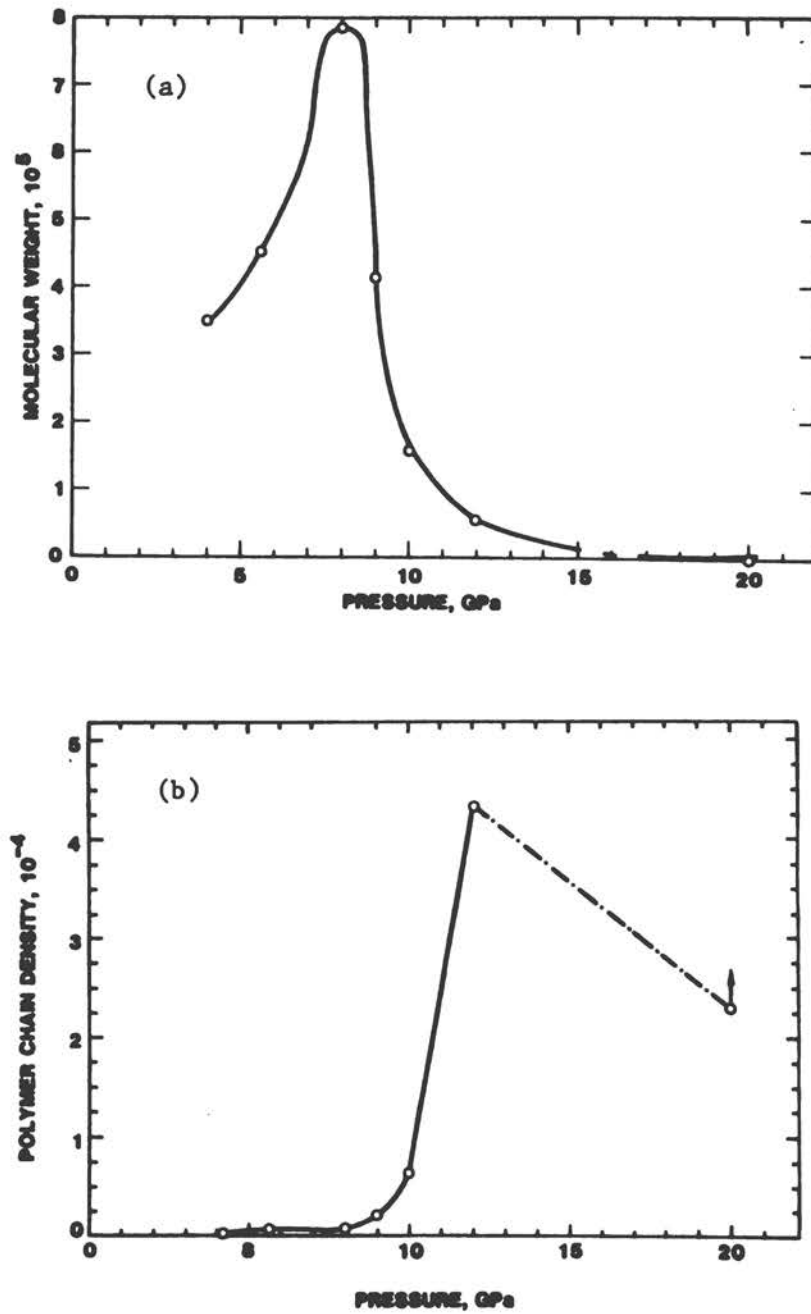
FIGURE 2-3.   Linear polyacrylamide molecular weight (a) and
polyacrylamide chain density (b) vs. shock pressure
for multiple-compression shock loading of acrylamide,
based on data from Ignatovich et al. [1970]. (The
20-GPa point on b is a lower limit only.) The
behavior of both quantities in the 9- to 11-GPa region
implies a major change in the polymerization mechanism.

In other work, Veretennikov et al. [1966] have measured the Hugoniot curve of polyacrylamide (PAM). It is very nearly coincident with the Veretennikov acrylamide (AM) Hugoniot between 1.8 and 5 GPa. It lies below the latter from 0 to 1.8 GPa and from 5 to approximately 8 GPa. The PAM curve has a cusp and a break in slope similar to that shown in Figure 2-1 for AM, but the cusp occurs at slightly higher pressure, approximately 8.5 GPa. The shock velocity-particle velocity Hugoniot curves (D, u curves) for AM and PAM are shown in Figure 2-4.
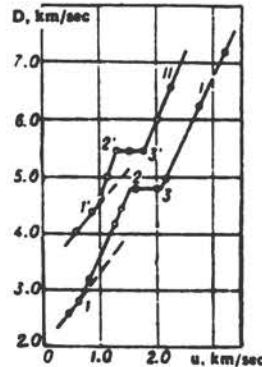
FIGURE 2-4.   D, u Hugoniot curves for AM and PAM [Veretennikov, Dremin, and Mikhailov, 1966].

A break in slope in this plane is commonly taken to imply the onset of a change in the physical or chemical state of the material. It is assumed [Veretennikov et al., 1966] that the break at 1 in Figure 2-4 corresponds to the onset of polymerization or to the formation of active centers leading to polymerization. The heat of polymerization of AM is approximately 15 kcal/mol. This corresponds to approximately 0.88 GPa cc/g. For $(\partial P/\partial E)_v = 2.22$ g/cc, this gives $\Delta P = 1.95$ GPa times the fraction of AM polymerized. For complete polymerization the offset between the unreacted AM curve and the completely reacted curve would be 1.95 GPa. The offset estimated from Figure 2-4 is 1.6 GPa. Veretennikov et al. [1966] also suggest that the transition region from 8 to 12 GPa corresponds to generation of cross-linking. Recovery experiments showed both cross-linking and "degradation" in this transition region.

The nature of the material recovered after shocking AM, and its variation with pressure, are described by Adadurov, Gol'danskii, and Yampol'skii, [1973]. The product is a mixture of a water-soluble fraction (SF) and a water-insoluble fraction (IF). The soluble fraction has been found from IR analysis to consist of a linear polyacrylamide (LPAM) and beta-alanine.

The IR spectrum of the IF has an absorption band at 1550/cm that is related to a secondary amide group, and the 1620/cm band normally found for the polymer is absent. The IF is therefore assumed to be a cross-linked PAM with amide bridges between the chains (XPAM).

As final pressure increases above the 2-GPa threshold, the ratio of XPAM to SF changes, the average molecular weight changes, and the total yield changes. The total yield increases very slowly from 2 to 5 GPa; it increases linearly to a maximum of about 52 percent at approximately 12 GPa, decreases to approximately 48 percent at 20 GPa, and falls to zero at 35 GPa. The yield of XPAM increases linearly from 4 to 20 GPa, where it represents almost the entire yield. The yield of SF has a maximum of approximately 22 percent at approximately 11 GPa and it decreases to about 4 percent at 20 GPa. The yield of beta-alanine rises from zero at about 5 GPa to approximately 27 percent at about 15 GPa. It falls to approximately 25 percent at 20 GPa and 12 percent at 35 GPa. (There are inconsistencies in various statements about yield, including those by Adadurov, Gol'danskii, and Yampol'skii [1973]. In Veretennikov, Dremin, and Mikhailov [1966] give the yield as 60 percent at 7 GPa. Babare, Dremin, Pershin, and Yakovlev [1970] reported that no polymer was recovered in single shock compressions to 2.5, 5, or 8 GPa.)

SF and IF are believed to be formed simultaneously, not sequentially. The basic process is described as vinyl polymerization below 6 GPa. Above 6 GPa the contribution of migration polymerization increases.

In a more recent article Adadurov and Gol'danskii [1981] reported experiments on the polymerization of acrylamide at various initial temperatures for both SW and DIC loading. Initial temperature had a large effect on yield for both types of loading. The yield with SW loading was characteristically 5 to 10 times that obtained in DIC loading, except at room temperature and 40 GPa. There the sample was totally degraded by SW loading, but the yield with DIC loading was 20 percent.

Veretennikov, Dremin, and Mikhailov [1966] reported that a series of experiments was carried out in which duration of the compression time was varied from fractions of a microsecond to several microseconds. A close relation between polymer yield and duration was reported, and no polymer was recovered for very short durations, even for quite strong shocks.

Dodson at Sandia Laboratories [Dauben, 1983] has reported that, in plane impact experiments with SW loading to 4.8 and 6.7 GPa, no polymer was recovered. But activation centers had apparently been created, because polymerization occurred when the recovered sample was placed in solution. This leaves unanswered the question whether polymerization results from the shock or post-shock stage.

DISCUSSION

Since no commercial polymer synthetic processes based on shock processes now exist, and since none are proposed, we consider here only the scientific issues raised in literature from the USSR and in work in the United States and Japan described at the workshop held by the committee.

From the point of view of chemical kinetics, a propagating shock wave is a nonlinear collective process consisting, in simplified form, of a rapid rise in density and temperature, a "quiescent" period of as much as several microseconds at high density and temperature, and a less rapid decompression period. The actual rise-time is theoretically dependent on shock magnitude and material composition and lies in the range of 10^{-8} to 10^{-12} seconds. At the shorter end of this range, shear forces having significant gradients on an Ångstrom scale should be present. Significant microscopic turbulence with resulting mixing may also be possible during the quiescent period. These microscopic fluid dynamic and shear phenomena remain poorly understood and have been but poorly demonstrated. Their existence must be labelled speculative until measurements and more complete theoretical work are available.

There is abundant evidence that chemical reactions occur during shock passage through organic solids and liquids [Babare, Dremin, Pershin, and Yakovlev, 1970]. Many unusual reactions, especially polymerization reactions, have been reported. One particularly striking example, which must certainly be independently verified, is the polymerization of liquid benzene to low yields of "polyacetylene." In some cases the polymers obtained are not those obtained under static pressure or via more conventional techniques. Almost all present knowledge of these shock reactions comes from final product analysis. General outlines of possible mechanisms are possible in some reactions. In no single case is the reaction mechanism, in the sense of a specific time-dependent sequence of intermediate species, known and experimentally verified, although it is possible in some cases to rationalize the process in terms of perfectly normal chemical pathways. For example, one can view the polymerization of acrylamide as a free-radical polymerization, in which the initiating species are free radicals produced by the intense shear stresses accompanying the shock front, and the molecular mobility in the monomer crystal necessary for the chain reaction to continue is provided by the stress decay behind the shock front. Having said this, it still must be recognized that there is no theory, either fundamental or empirical, that gives even semiquantitative insight to the final products.

The shock wave presents a unique sequence of processing steps, and it is possible that many of the unusual reactions uncovered to date could be successfully analyzed in terms of ordinary chemical kinetic concepts, if the appropriate rate constants at high density and temperature were available, and if our understanding of the shock's physical nature were complete.

It is also possible, yet certainly not experimentally demonstrated, that novel excitation and reaction processes occur at the molecular level. One open question is the rate of equilibration of internal vibrations with center of mass energy as the shock wave passes. Spectroscopic measurements on a simple molecule, carbon disulfide, suggest that in this case equilibration requires the order of 10^{-7} second. For shock front rise times of 10^{-8} to 10^{-9} second and relatively large organic molecules, our present understanding of these processes suggests that internal vibrations will adiabatically follow the local thermodynamic variables.

In the limit of 10^{-12}-second rise times, however, the redistribution of vibrational energy might be slow with respect to shock-front passage. In this limit an individual molecule could simultaneously experience significant shear. In this situation reactions might not follow the normal Arrhenius and RRKM-type mechanisms.

In mechanochemistry [Casale and Porter, 1978], static stress and shear forces on solid polymers are found to cause reactions. While detailed mechanisms are not known, it is thought that force fields dependent on molecular topology can cause specific bonds to break. The weakest bond does not necessarily break first. Similar phenomena may occur on short time scales in shock fronts.

After passage of the shock front, unimolecular and bimolecular reactions may occur for approximately 10^{-6} second at high density and/or temperature. In the dynamic isentropic method [Adadurov and Gol'danskii, 1981] coupled with precooling of the sample, high density at temperatures below room temperature can be achieved. Unusual reactions may be observed here simply because regions of the ground state potential energy surface that are not accessible at lower densities are now populated. Species present at the end of the approximately 10^{-6}-second period of high density can be "frozen in" by a rapid decompression. There is indirect evidence for enhanced transport mobility during this period of high density, and microscopic turbulence may play a role here. There is direct evidence for the presence of strong electric fields during this period, principally in polymers of complex monomers [Graham, 1979]. Ions as well as neutral radicals are apparently created in the shock front. The entire subject of microscopic behavior in this regime is in an uncertain state and great effort will be needed to bring coherence and understanding to the problem.

RECOMMENDATIONS

Two questions were posed in the Preface of this report which provide motivation for the report and its recommendations: Does shockwave chemistry hold technological promise? and does it provide opportunity for obtaining important new insights into the science of chemistry? In the case of organic chemistry it seems reasonably clear at this time that no assessment of the technological promise can be made until a much

better understanding of the microscopic aspects of the shock compresssion process is obtained. For this reason, the following recommendations are directed principally toward the second question.

To assess seriously whether important new chemical principles are involved in shock compression polymerizations we require much more thorough characterization of the starting materials and products of the shock compression at minimum and ideally of the chemical events in the shock front itself in real time.

The purity of the starting materials can have important effects in conventional polymerization, and similar effects should be anticipated for shock compression polymerization. For example, the low yield of polymer product from benzene is conceivably due to polymerization of thiophene impurity. A complete specification of the chemical impurity levels in the starting monomer is essential.

At the same time, the products of the shock compression must be more carefully analyzed. It is important to know the molecular weight distribution, degree of branching, stereoregularity and head-to-tail regularity of the polymer product as well as some average molecular weight. One should also analyze the nonpolymer components of the recovered samples to see what side reactions have occurred. Chromatography of the soluble fraction is important and seems not to have been reported by any investigation to date. Determination by ESR of trapped free radicals remaining in the product after shock compression and monitoring their behavior during subsequent processing also would be useful. X-ray and scanning calorimetric analysis of crystalline monomer and polymer products of the shock process would give additional information on the defect character of the shock product.

Contamination of the sample by the metal container has been of concern to Soviet scientists, and in one case the product was found to contain as much as 14 percent copper [Yakushev, Nabatov, and Yakusheva, 1974]. It would be appropriate to apply surface analysis for trace metals (by EDAX or Auger) and their ionization state (by Auger) to determine whether any catalytic activity is added to the organic reactants by such impurities.

Ideally, in order to come to firm conclusions about the chemical mechanism involved, one should couple the more complete characterization of shock compression product with methods for determining the progress of the polymerization reaction in the shock front itself. This should be done in model systems chosen at this stage for ease of characterization rather than for ultimate properties. Such studies would help to describe mobility during the period of uniform pressure behind the shock front and to identify reactive species created by the shock front. Optical absorption/emission experiments, as well as resonant and coherent Raman spectroscopies, have considerable promise for following polymerization in real time during shock compression [Ogilvie and Duvall, 1983; Moore,

Schmidt, and Shaner, 1983; Schmidt, Moore, and Shaner, 1983].
Unfortunately, these latter two techniques are still far from routine and involve expensive and sensitive optical components that may be incompatible with the environment in which the shock experiment is carried out. As a longer range goal it might become feasible to use picosecond laser techniques to look directly into the shock front. Experiments in which the shock compression is carried out by laser vaporization of an absorbing thin film [Campillo, 1983] rather than by conventional explosive methods would seem to offer more compatibility with optical spectroscopy and the best promise for success here.

In the absence of definitive evidence of unusual chemical effects of shock-produced polymerization, it seems wise to concentrate on a few model systems that can reveal the basic principles. These should be systems whose photochemistry and thermochemistry are well understood for a wide range of static pressures and temperatures. Even in such a system, it should be possible to vary the state of the starting monomer system from a liquid well above its glass transition temperature T_g to one just above T_g, to a glass, and finally to a crystalline state. If the intense shear accompanying the shock front is important in initiating and sustaining the polymerization, as seems likely, these changes in state should have important effects on polymerization reactions. The intriguing possibility of selective bond scission of the monomer by crystallographic shear of the monomer crystal can be explored, as can the possibility of obtaining new stereoregular polymers from the same selective shear where the stereoregularity is inherited from the structure of the monomer/crystal. Any such effects that may survive the potential disordering of the monomer crystal by shock compression should be compared with what can be produced by conventional initiation procedures (e.g., photochemistry).

The experimental program should be accompanied by relevant theoretical studies and numerical modeling. The following areas are of particular importance:

1. Analytical and numerical computations required to accurately determine the stress and temperature histories of recovered samples. This necessarily implies the construction of accurate and reliable equations of state for experimental materials and the reaction products.

2. Extension of molecular dynamic calculations to provide a conceptual framework for reactions due to shear and momentum impulse forces in the shock front.

3. Ab initio quantum chemical calculations for model systems used in future experiments. These should explore particularly the effects of shear and torsional deformations of molecules.

4. Since knowledge of temperature in shock waves is poor, close attention should be given to the problem of temperature measurement, with exploration of possible methods for in situ measurements of temperature.

3. INORGANIC CHEMISTRY

STATUS

Most work on chemical changes, material synthesis, and material modification induced in inorganic substances by shock compression has been carried out with powder-compact samples. Typical powder compacts are composed of particles whose sizes range from a micron to tens of microns and are pressed or otherwise consolidated into a coherent body whose density ranges from 40 to 65 percent of solid density. Because of their porosity, these powder compacts cause shock-loading conditions in which details of local stress, stress configuration, compression, temperature, and temporal behaviors are considerably more difficult to define than in a fully dense body. Nevertheless, from both fundamental and technological viewpoints, the most compelling experimental results have been obtained on powder compacts, and it is necessary for scientists engaged in future studies to accept detailed description of local shock compression conditions as an unresolved but important challenge.

The earliest exploratory work was often carried out by investigators more concerned with technological innovation than with fundamental science. In the Soviet Union Riabinin [1956] reported the first shock-induced chemical reactions with observations of decomposition of $CuSO_4$, $MgCO_3$, and $Pb(NO_3)_2$. In 1961 U.S. scientists DeCarli and Jamieson reported the first successful shock synthesis of diamond from graphite [DeCarli and Jamieson, 1961]. After taking some years to develop, the industrial demand for shock-synthesized diamonds is now flourishing. In 1963 a mixture of zinc and iron oxides was shocked to produce $ZnFe_2O_4$ [Kimura, 1963], and shocking a mixture of titanium and carbon produced titanium carbide [Horiguchi and Nomura, 1963]. These were the first reports of compounds having been synthesized by shock wave action. In 1966 Bergmann and Barrington reported an extensive study of shock modification of a number of inorganic powders and presented evidence for shock-enhanced densification in sintering [Bergmann and Barrington, 1966]. In 1965 Horiguchi and Nomura reported that shock modification of acetylene black greatly increased its catalytic activity [Horiguchi and Nomura, 1965]. Thus, during the period between 1961 and 1966, shock-enhanced solid state reactivity and direct chemical and direct structural synthesis had all been explicitly demonstrated.

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Except for commercial work on diamond synthesis, the early work was not continued in the United States, where mainstream fundamental research studies concentrated on improved physical understanding of the shock compression process. In the United States, shock compression of condensed matter has developed as an area of physics, with only peripheral involvement of chemistry.

In the period between the middle 1960s and the late 1970s, scientists in the Soviet Union carried out major programs in shock-induced chemistry and material modification. Their work was highlighted by multidisciplinary efforts that included chemists and material scientists along with scientists knowledgeable in fundamental aspects of shock compression. This Soviet work has provided a broad, if somewhat shallow, base that outlines significant areas of research and consistently indicates the existence of enhanced solid-state reactivity and shock-induced chemical synthesis.

Table 3-1, taken from Batsanov [1978], lists and categorizes many of the reactions that have been studied in the USSR and, to a lesser extent, in Japan. It gives an idea of the scope and magnitude of work to date. Yields are not usually quoted, but the nature of the observation suggests that in some cases the yield is substantial: e.g., "elevated density."

Shock synthesis has been attributed to

1. Fracture of initial grains into submicron-size grains;

2. Creation and trapping of residual strain and related defects;

3. Reduction of activation energies by 1 and 2 above;

4. Temperature inhomogeneities;

5. Pressure- and temperature-induced increases in the electrochemical differences between the reagents; and

6. Containment of the samples in capsules that prevent disintegration and may contain appreciable residual pressure.

Other work than that listed in Table 3-1 includes the study of more than 60 oxide powders for shock-induced decomposition. For compression to 48 GPa it is found that those for which ΔH°_{298} is approximately less than 140 kcal/mol decompose. Those for which ΔH°_{298} is larger may be brought to a more highly ordered crystalline state by action of the shock waves [Adadurov, Gol'danskii, and Yampol'skii, 1973].

An extremely interesting effect of shock compression, and one that has important potential applications, is the activation of catalysts. For example, the rate of decomposition of H_2O_2 by carbon black is increased if the carbon is shocked before use [Horiguchi and Nomura,

TABLE 3-1. Shock-Induced Reactions in Inorganic Substances [Batsanov, 1978]

Sample	Product	Structure	Observation
	1. Solid solutions		
$KCl + KBr$		NaCl	Elevated density
$RbCl + CsBr$		NaCl	Independent of stoichiometry
$NH_4Br + CsBr$		CsCl	First observation
$NH_4CL + CsCl$		NaCl	First observation
$NH_4I + CsI$		NaCl	Miscibility increases with $I > Br > Cl$
$NH_4X + KX$		NaCl	
$W + Fe$		Fe	Unlimited miscibility
$Mo + Al_2O_3$		Al_2O_3	Not formed thermally
$SiC + Al_2O_3$		Al_2O_3	Not formed thermally
	2. Interaction of oxides		
$ZnO + Fe_2O_3$	$ZnFe_2O_4$		
$ZnO + SiO_2$	Zn_2SiO_4		
$Zn_2O_3 + H_2O$	$ZnOOH$		
	$AnOH_3$		
$Al_2O_3 + SiO_2$	$Al_2(SiO_3)_3$		
$CaO + Cr_2O_3 + SiO_2$	$CaCr_2Si_3O_{10}$		
$BaCo_3 + TiO_2$	$BaTiO_3$		
$MgO + SiO_2$	$MgSiO_3$		
$CaO + SiO_2$	$CaSiO_3$		

TABLE 3-1 (cont'd)

Sample	Product	Structure	Observation
	2. Interaction of oxides (cont'd)		
$PbO + TiO_2$	$PbTiO_3$		
$PbO + ZrO_2$	$PbZrO_3$		
$PbO + TiO_2 + ZrO_2$	$Pb(Ti,Zr)O_3$		
$SmO + TiO_2$	$SmTiO_3$		
	3. Molecular synthesis from the elements		
$Ti + C$	TiC		
$W + C$	WC		
$Al + C$	Al_4C_3		
$Cr + S,Se,Te$	CrY		
$Sn + S,Se,Te$	SnY		
$Sn + Nb$	Nb_3Sn		
$Al + Nb$	Al_3Nb		
$Ho + S$	Ho_2S_3		
	4. Synthesis with change of valence		
$Cu + CuBr_2$	$CuBr$		Reduced cell parameter
$Ti + TiO_2$	TiO		NaCl structure
$In + InF_3$	InF_2		New modification
$Ln + LnF_3$	LnF_2		Obtained for the first time, CaF_2+ structure
$Cu + CuO$	Cu_2O		Normal modification
$Mn + Cr_2O$	$MnCr_2O$		Reduced cell parameter

1965], and the rate of oxidation of CO by TiO_2 is increased 100 to 1000 times if the TiO_2 is first shocked [Batsanov, Bakhmutskaya, Deribas, and Zalivina, 1967]. (While these few observations do not automatically suggest the outlines of a complete study of catalysts, they are promising enough to warrant greater consideration. Furthermore, it must be recognized that a successful catalyst requires not only increased activity but also increased selectivity, as well as reproducibility and in situ regenerability.)

An area of inorganic chemistry that has developed aside from the mainline research described above and largely outside the USSR involves the geophysics and geochemistry of meteorite impact. A substantial body of literature on impact-produced structures and transformations forms the basis for relatively standard identification and classification procedures for meteorites or suspected meteorites [Boctor, Bell, and Mao, 1982].

Dynamic measurements on inorganic substances are of the same kinds as those described for organic materials. They include

o   Mechanical measurement of elastic failure amplitude in solids and its relation to dislocation properties;

o   Identification from Hugoniot data of physicochemical transformations in liquids and solids that convert material to states of greater density;

o   Electrical conductivity;

o   Electrical polarization;

o   Electrical signals generated by physical or chemical transformations;

o   Bleaching of optical defects in alkali halides;

o   Reflection and absorption of light;

o   Light emission; and

o   Absorption and reflection spectra.

The action of shock waves in inorganic liquids is different from that in solids. Very little has been done with inorganic liquids; water, liquid argon, xenon, hydrogen, nitrogen, and carbon disulfide are exceptions. There are interesting fundamental problems associated with their shock compression, but they have been relatively little studied. Among solids it is important to recognize the differences between competent or compact solids and powders or porous solids.

Compact solids--e.g., single crystals or poly-crystals--suffer mechanical failure if they are shocked to sufficiently high pressures. Mechanical failure in such cases is believed to consist of yielding and plastic flow in metals and in some, if not all, insulators and semiconductors. There is no direct evidence of fracture under the influence of the shock front or the compressed state that follows. There is evidence to suggest that heterogeneous yield and localized melting may occur in some insulators, but this is still being studied. It is reasonably certain that large numbers of defects are produced in the compression phase of the shock wave, but not necessarily in the shock front.

It is important to recognize that, although the rise time of the shock is very short, the processes initiated by the shock front may take long times (i.e., microseconds) to run their course. It is almost certain, for example, that dislocations, driven by shear stresses in the shock, do not multiply in the shock front, although nucleation may occur there. Multiplication takes place in the region behind the shock front. Less is known about formation of point defects and vacancies, but it is likely that the same is true for them [Dick and Styris, 1975]. And, of course, large-scale defects must take very long to form, so it is unlikely that extensive changes occur in the shock front itself, although the seeds for change may be sown there. This view is supported to some extent by dynamic X-ray diffraction measurements, including shock fronts, which give direct evidence of crystalline order behind the shock front [Johnson, Mitchell, and Evans, 1971].

There is little question but that most of the macroscopic fracture damage experienced by recovered shocked solids occurs after the shock front has passed, pressure is being relieved, and the tensile and shear waves generated by bounding surfaces begin to reverberate through the specimen. The extent to which defects and heterogeneous melting contribute to the final fractured product is unknown.

The situation is quite different in powders. The surface area in unit volume of a fine powder is about 10^5 times that of a solid. Surfaces produce rarefactions, and interacting rarefactions may cause fracture. Individual grains in a powder are not subject to uniaxial strain. They have very complicated stress loadings and strain patterns thrust upon them by their neighbors. They may also experience very high surface temperatures from friction, heating of gas in pores, jetting, etc.

It is known that both particle comminution and particle agglomeration are strong functions of shock pressure. Crystallite size as indicated by X-ray diffraction line broadening is strongly material-specific, and reductions in crystallite size typically occur only above pressures of about 10 GPa. Point and line defect concentrations increase to extraordinarily large values at pressures ranging from 5 to 25 GPa. Because of the shock-induced temperature rise, residual defect concentration may be reduced below the value existing immediately after

release of pressure. Residual strain due to the presence of imperfections represents stored mechanical and thermal energy and may influence reactivity beyond that resulting from enhanced mobility due to the presence of defects. Particle morphology can strongly influence reactivity, and there are indications that shock-activated powders show extraordinarily chemically active surfaces [Batsanov, 1967; Adadurov, Gol'danskii, and Yampol'skii, 1973; Adadurov and Gol'danskii, 1981; Morosin and Graham, 1981].

All of the effects listed have been characterized to a certain degree, but the key issue of relating shock-induced modification to enhanced reactivity is a difficult one requiring considerable careful research. The degree of modification experienced by powders subjected to shock compression may be outside the range of conventional experience, and expectations of material response based on conventional concepts may be far different from observed results.

The shock front in a powder is quite thick, being of the order of the grain size. So the powder, unlike the solid, has excellent opportunity to suffer the total range of distortions, fractures, consolidation, melting, etc., during the initial and subsequent compression period. The subsequent rarefactions break it apart, as pointed out by Wilkins [1983].

Most interest in inorganic shock chemistry has been in powders, as suggested by Table 3-1. In these experiments it has been found that shock compression lowers the temperatures at which phase changes or chemical reactions occur and increases the solubility or absorptivity, or it may improve the sintering performance. Whatever the effect, it is normally a rapidly rising function of shock pressure reaching a maximum at some pressure greater than 10 GPa and falling less rapidly at higher pressures as a result of the high temperatures associated with very large pressures, Figure 3-1. These observed changes in activity are almost without doubt a consequence of the various damage processes occurring in the shock front and beyond, as discussed earlier.

Entry to the literature on this subject can be gained through the references listed and also through the bibliography by Graham, Morosin, and Dodson [1983].

DISCUSSION

Any discussion of shock-induced inorganic chemistry should distinguish among several chemical transformations that shock can produce:

1. Phase transformations;

2. Chemical decompositions;

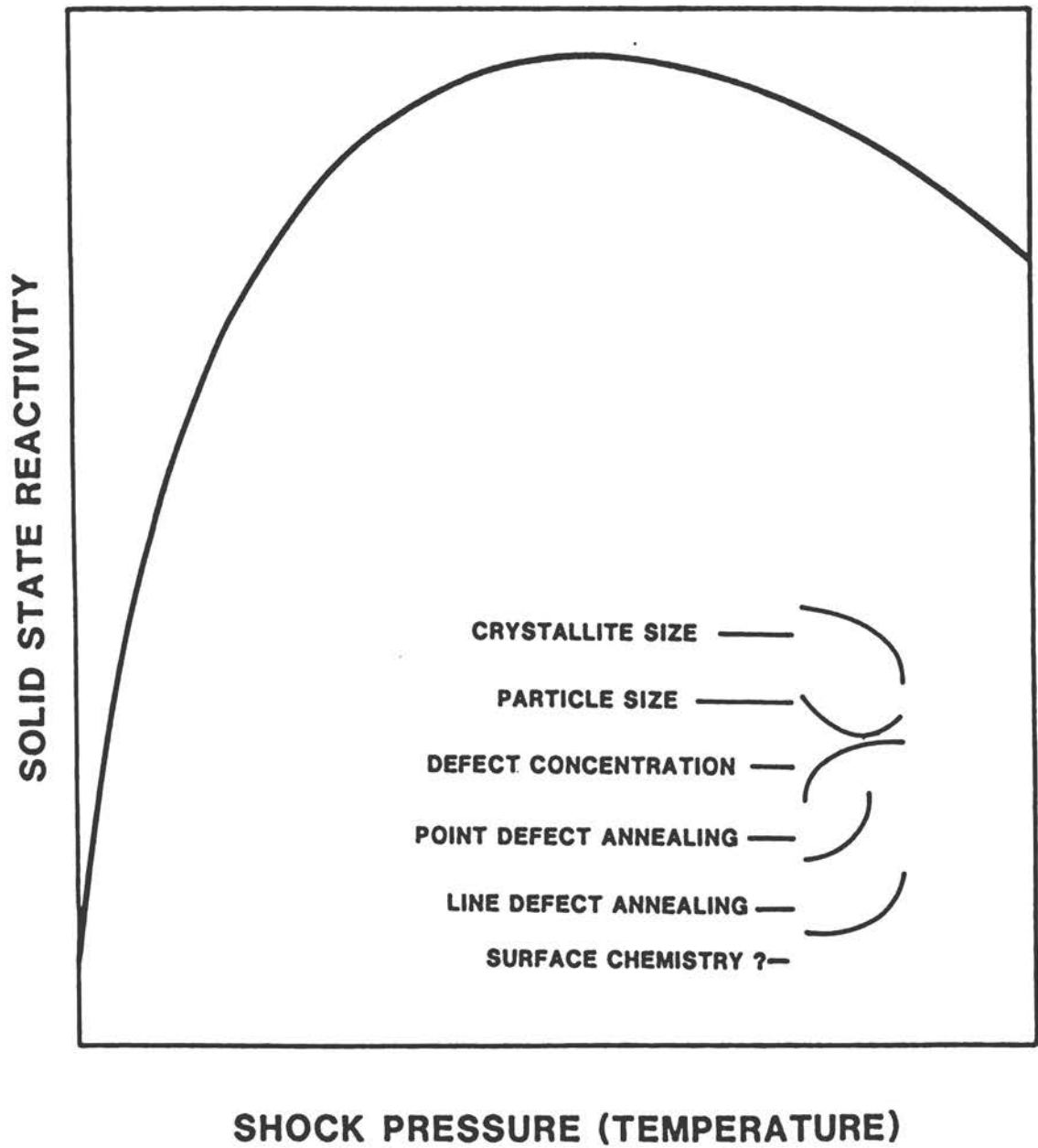3. Chemical syntheses during shock compression;

FIGURE 3-1.   Effect of shock compression in powders.

4. Shock-activated post-shock chemistry; and

5. Compaction.

This commentary concerns the first four processes; compaction is briefly considered in Chapter 4.

Phase Transformations

Shock-initiated phase transformations to structures that are metastably recovered are the bases of two commercial applications of shock compression: production of diamonds and cubic boron nitride. In both cases, chemical bonds are rearranged during the transformation. Both processes use reagents (graphite and hexagonal BN) with the same local compositions as the products; neither process transports atoms between inhomogeneous phases during the brief interval the sample is compressed. The products are microcrystalline. Careful study of variation of conditions for producing these materials might yield a direct return in terms of improved product and an indirect one of better understanding.

Chemical Decomposition

Chemical decomposition occurs during shock compression of many materials that are thermally unstable at low pressures (explosives provide the best known and most dramatic examples; there are nonexplosive materials also—e.g., MgO_3 and other carbonates or hydrous solids). In these reactions, all reagents are at the reaction center before compression, so transport is not a problem. However, a few inorganic decomposition processes have been identified that cannot be duplicated by other routes. Decomposition appears to be more of a potential problem for shock synthesis than an advantage.

Chemical Synthesis

Chemical synthesis of unusual inorganic alloys and compounds from heterogeneous compacts of two or more compounds is difficult but not impossible under shock conditions. One example is the preparation of superconducting compounds—e.g., the A15 form of Nb_3Si with high T_cs—by this method [Olinger and Newkirk, 1981; Okshima et al., 1981]. Syntheses of several more complex materials from ceramic powders (e.g., $PbZrO_3$ from PbO and ZrO_2) have been attempted with some success. Thus, mass-transport barriers can be surmounted in some cases [Gal' et al., 1979]. However, syntheses in ceramic systems often are reported to have yielded irreproducible quantities of inhomogeneous products with significant amorphous or unreacted material.

It would be of great interest to synthesize certain unusual inorganic compounds, like $(Si,C)O_2$; yet the value of synthetic work described in the literature for future studies is difficult to project. The starting

materials for many reported syntheses were mixtures of finely divided
powders in order to surmount mass-transport barriers to reaction. The
reactivities of fine powders under shock compression should be very
sensitive to surface contaminants and may even be sensitive to surface
defects in the pre-shocked material. Many different potential changes
can occur in these materials during shock compression [Okshima et al.,
1981; Olinger and Newkirk, 1981], but the nature and magnitudes of these
changes are only slightly understood, even for single-component
ceramics. Furthermore, in most of the reported syntheses the states of
the starting materials were poorly characterized at best. The
quantitative data needed to design more efficient processes are
effectively unavailable.

The paucity of basic data about transformations of simple systems has
led many investigators to shelve synthetic work, at least temporarily, in
favor of experiments directed toward understanding shock-induced
modifications and defect production in one-component systems. However,
results described to the committee suggest that, in many of these
studies, the microstructures of the starting materials and products have
been inadequately characterized. The risk of such inattention is that
these studies also will be impossible to interpret. When compared to the
funds already expended to obtain uninterpretable results, the cost of
appropriate microstructural analyses for several model systems is small.

Post-Shock Chemistry

Several reports have described "shock activation" of post-shock
catalytic activity and enhanced sinterability, which are presumed to
result from high concentrations of defects produced during the shock
process. A particularly interesting example is the catalytic activity of
TiO_2 mentioned in the preceding section. Formation of color centers
and shear structures by shock suggests chemical reduction, with
separation of Ti from O. Color centers thus formed disappear by
annealing in N_2. It is suggested that this occurs by recombination of
TiN with O retained in the sample, but it could occur by formation of TiN
through reaction of Ti with N_2.

The question of enhanced sinterability is also an interesting one, to
be addressed in Chapter 4. However, to understand it, as to understand
the catalytic effect, requires detailed knowledge of the post-shock
state, and here again characterization of the microstructural
transformations in the shocked material has been limited.

RECOMMENDATIONS

The status of research in inorganic materials is somewhat different
from that of organic materials, described above. Here there is some
technological promise, which provides incentive for a frontal attack on
specific synthesis problems. There are also many basic scientific

questions to be studied if the technological promise is to be realized and optimized. The importance of both these questions provides motivation for the following recommendations.

To be able to interpret product yields, one must know the condition of the surfaces of the reagents. The presence or alteration of specific surface defects and contaminants may significantly affect yields and properties of the products and should be examined. Characterization of the surface states of the products may provide valuable clues about mechanisms of shock-induced reactions.

Surface analysis of shocked materials is probably the most easily added analytical tool that will provide useful characterization of these systems. In the cases of high-surface-energy powders, for example, removal or alteration of surface contaminants may be found to contribute to the behavior of shocked systems. Formation of active sites on surfaces or creation of microcracks that can aid in the flow mobility required for sintering are all possible. The analytical techniques that should be applied include scanning electron microscopy with EDAX, Auger spectrometry for regional elemental analysis, and, if organics are present, FTIR and XPS (ESCA). For crystalline or semicrystalline materials, surface crystallographic techniques such as LEED or RHEED may prove valuable for assessing alterations of surface order as a result of shock and also could be used to monitor annealing reactions of shocked materials to obtain insight into the nature and reversibility of shock-induced states.

In future work, surface analyses should be carried out to detect surface states, increases of surface area, or other microstructural changes that correlate with enhanced reactivity. In general, SEM is the easiest method to apply. Other UHV techniques are more difficult to use with fine powders, since many UHV investigators also are reluctant to "contaminate" their apparatus with samples of unknown composition. One response to this problem is to design shock experiments with pre- and post-analysis in mind; for example, single crystals of ultrapure metals or ceramics of known composition and particle size might be studied. Another important area for innovation is in situ analysis during shock compression by a variety of laser spectroscopies. Promising initiatives in this area have been taken by Schmidt and Moore at Los Alamos Scientific Laboratory [Schmidt, Moore, and Shaner, 1983; Schmidt, Moore, Schiferl, and Shaner, 1983]. More speculative, but also interesting, is the attempt being made by Campillo and colleagues at the Naval Research Laboratory to synchronize laser-produced shocks with laser diagnostics [Campillo, 1983]. The task is beset with problems, but it would be a very valuable addition to analysis, were it to succeed.

At this stage in the investigations it would be most valuable to concentrate efforts on thorough examination of a limited number of model systems. The aim should be to carefully characterize the kinds and extent of microstructural changes produced by shock compression.

Specifically, funds should be provided to implement adequate pre- and post-shock surface characterization of the sample. Adequate time on suitable instruments will have to be purchased. Just as important is providing funds to implement the computations and experiments required to accurately characterize the shock environment.

The problem of mass diffusion over relatively large distances in very short times pervades this issue of inorganic synthesis. Diffusion coefficients have been variously reported as 100 to 1000 times greater than normal values [Zemsky, Ryabehikov, and Epshteyn, 1979; Batsanov, 1979]. This is a question of central importance. It should be addressed experimentally under carefully controlled conditions. It appears to have features that make it amenable to molecular dynamics modelling, and it should be examined to see if a meaningful computation can be made.

The role of temperature in these experiments is certainly significant. Since there do not now exist methods for in situ measurements of temperature in shock waves, efforts should be made to develop suitable techniques for making them.

4. COMPACTION AND SINTERING OF POWDERS

"Dynamic Compaction" refers to the operation wherein a powder is arranged in the geometry of the desired product and shocked by explosion or impact. The shock heats the powder and compacts it, producing, ideally, a competent bonded mass with shape, size, strength, and density suitable for the final product. In favorable situations it is possbile to carry out this process if the finished article has a simple shape--e.g., a cylindrical shell as described by Wilkins [1983]. To accomplish this, it is necessary to know the details of the shock-induced motions on a fine scale. The knowledge that has been acquired about these motions from wave code calculations, for example, is useful in designing experiments aimed at greater understanding of shock processes in powders, including those of chemical reaction and diffusion.

The shock compaction process is so brief and intense that compacted bodies of relatively unstable materials can be formed, e.g., amorphous metals. At present this is the only known method for preparing such things. Cracking of the final product, from either thermoelastic effects or interaction of rarefactions, is one of the principal problems to be overcome.

"Shock-enhanced sintering" refers to either of two processes. In one the process of dynamic compaction is carried out, as described in the preceding paragraphs. The resulting compact is subsequently compressed and heated statically by normal sintering procedures to produce the final product. An important advantage of this procedure is that the density of the dynamically compacted item is greater than that of specimens normally prepared for sintering.

In the second procedure, the powder is shocked in any convenient geometry, remilled, and then sintered. This "shock conditioning" appears to give a superior final product for some materials and not for others. One hope is that sintering of difficult materials--e.g., SiN--may be achieved without additives, which weaken the final product.

The shocking process adds free energy in the form of vacancies, dislocations, etc., to particles, and this accelerates diffusive processes involved in sintering. These effects might be useful in the preparation of sintered bodies in which deleterious side reactions

compete with the sintering process. It is possible to improve the sintering behavior of many materials by pretreatments other than shock compression, and, so far, commercial presintering shock treatments have not been widely used.

In Japan, Sawaoka and others have combined the processes of shock compaction and sintering. Graphitic BN has been confined in a copper sleeve, shock-compressed, and recovered as a cylinder of BN that is mainly in the dense, wurtzitic form. This material was subsequently statically hot-pressed at about 1400°C and 5.5 GPa to form strong bodies of mostly cubic BN that may be useful as cutting tools, etc. Whether this process is commercially attractive or not remains to be seen and depends partly on the value of the product [Sawaoka, Soga, and Kondo, 1982; Sawaoka, 1983].

For many years the DuPont Company has been making fine particles of diamond by shock-compression of graphite. This diamond is useful as an abrasive for lapping and polishing, but its small particle size prevents its use for more severe grinding operations. Attempts have been made to sinter this powder at high pressures and temperatures to make cutting tools, etc., but so far no success has been reported along these lines.

An important element in both dynamic compaction and shock-enhanced sintering appears to be the fracture, defect structure, and associated deformation of the shocked powder. This implies an urgent need for detailed characterization of the defect state of shocked powders. It is important to know whether the defects formed are the familiar catalog of point, line, and planar defects known from quenching, irradiation, and straining experiments, or whether new defects are formed. This issue is both scientifically interesting and practically important, as the answer affects how one proceeds to make sinterable powders using this approach. Since defect physics is a highly developed and venerable field, it should be possible to make considerable progress in addressing this question from a base of solid understanding.

The need for surface characterization of shocked powders is also clearly an urgent one. Such questions as the formation of new electronic states at the surface as a result of slight elastic displacement, and the density of intersection of dislocations with the surface imply that the problem of atomic-scale reconstruction of the surface by the shock needs to be addressed. The problem is complicated by the irregular shape of the surface, but some tools are available.

For example, a shocked powder of a semiconductor, which might be recovered as a loosely bonded slug, could be studied by electrochemical means, which would reveal bond bending at the surface. Or the surface energy of the shocked compact could be studied by liquid metal infiltration; the degree of penetration (rise) would be a measure of the surface energy of that system.

The usual surface probes (XPS, SIMS, Auger) could be applied, but with the reservation that the information could only be qualitative, in view of the irregularity of the surfaces. In that regard, a model experiment in which spheroidized particles (made by dropping powder through a plasma) are compacted might be interesting. The particle-particle contacts would then be better defined.

The question of the temperature in the compact produced by shocking is a difficult one. Perhaps a thin film of a metal could be deposited on the particles in advance, and, following shock, evidence of melting of this film would be sought in SEM examination. By raising the stress level systematically, one could determine what level is required to give a surface temperature of the grains equal to the melting point of the metal.

The importance of stress-induced electric fields in insulating specimens also deserves attention. High local fields might affect defect production and chemical reactivity in the process zone [Mineev and Ivanov, 1976].

Shock experimentation should be supplemented by variations of conventional methods--e.g., ball-milling at elevated temperatures where shear and high local temperature are combined--to determine whether shock conditioning results can be duplicated by other means.

Other than these suggestions on procedure, we make no formal recommendations concerning sintering. We endorse the recommendations of the earlier report of the Committee on Dynamic Compaction of Metal and Ceramic Powders [1983], noting an important difference between dynamic compaction and the rest of shock chemistry: There appears to be a ready market for the products of powder compaction and sintering in both commercial and military applications.

5. FUNDAMENTAL PROCESSES

STATUS

It has been realized for more than 70 years that shock compression involves irreversible mechanical and thermal processes. Concern about the possibility of there being significant deviations from the mechanical and thermal states calculated from the equations of continuum mechanics dates from at least 1944. The capability of doing large-scale simulations of the shock process in condensed matter has existed for 20 years or more, but it is only recently that serious attention has been focused on this problem. It is particularly germane to the question of processes in shock wave chemistry, where Graham has emphasized the possibility that condensed-phase shocks are "catastrophic" rather than "benign" [Graham, 1979]. This means that atomic velocity distributions induced during shock wave compression are so far from equilibrium that chemical kinetic calculations based on equilibrium distributions of states would be seriously in error. There is now abundant evidence that Graham's catastrophic shock waves are real. Because shock waves do involve highly nonequilibrium states, there is potential for manufacturing unusual compounds. Klimenko and Dremin [Dremin and Klimenko, 1981] have stressed the likelihood of nonequilibrium effects and supported their ideas with calculations. They point out that, in trinitrotoluene, a shock wave generating a final temperature of 1000 degrees Kelvin can produce transient bond temperatures of a few electron volts. The underlying calculations are semi-empirical and crude, but the results are interesting enough to merit critical study. Because the potential importance of these effects is large, a more detailed analysis of shock wave structure is necessary. Monatomic fluids, polyatomic fluids, and solids have to be considered separately, because shock wave structure is sensitive to the microscopic makeup of the shocked material.

The shock transition is a nonequilibrium process that links together two quasi-equilibrium states. For a simple monatomic material in the fluid state, the nonequilibrium region has a relatively simple structure--the pressure tensor and heat flux variation can be understood from the standpoint of the Navier-Stokes equations of hydrodynamics. The accuracy of that picture has been established experimentally for dilute gases and by computer simulation for dense fluids [Hoover, et al., 1980]

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(Figure 5-1). From the chemical standpoint it is important to notice the substantial difference between the longitudinal and transverse temperatures (Figure 5-2). This work has shown that the rise time of a strong shock wave is about equal to the time between collisions. In a dense fluid, where the mean free path is only 0.2 nm and atomic velocities are of the order of kilometers per second, a rise time of about a picosecond would be expected. This estimate has been verified numerically [Hoover et al, 1980; Dremin and Klimenko, 1979].

In polyatomic fluids the shock wave structure is more complicated for two separate reasons. First, the parts of each molecule are excited sequentially during the time required for a stress wave to traverse it. Second, the molecular distortions generated by this excitation may take long times to equilibrate. In the extreme case of diatomic molecules, the relaxation time for the equilibrium of translational, rotational, and vibrational degrees of freedom behind a shock can be of the order of nanoseconds. This suggests [Johnson, Shaw, and Holian, 1984] that under shock wave conditions reaction pathways can be enhanced--for paths close to readily excited modes--or inhibited--for paths accessible only with difficulty. Although large molecules with many intermediate frequencies will transfer energy from mode to mode more easily than diatomics, quantitative liquid-phase estimates would have to be based on computer simulations.

The concept of isotropic thermodynamic temperature may not be sufficiently descriptive for polyatomic cases if chemical reactions are involved. It is difficult to treat the equilibration problem numerically, because of the lack of practical quantum dynamical simulations for more than two bodies. Soviet work [Dremin and Klimenko, 1981], which attempts to analyze molecular wave-function response to conformational changes, is very crude but suggests a potentially valuable approach to these problems. It appears that quantitative calculations lie well beyond the horizon.

In solids the complexity of the fluid is compounded with many inhomogeneities. There is no doubt that even fairly pure monatomic crystals can flow inhomogeneously along slip bands, with characteristic spacing on the micron scale. This is a consequence of instability. Hotter material is softer and concentrates flow. Additional complexities arise from grain boundaries, voids, inclusions, and mechanical anisotropies. Even if the problem of understanding a polyatomic fluid under shock conditions could be solved, the solid would be more complicated. Guidance from theory is meager. Martensitic transitions have been seen in computer simulations [Straub, Holian, and Swanson, 1980], but it is not feasible to simulate samples of macroscopic size. A feasible approach here would center on the study of relatively simple point or line defects. Because intramolecular and intermolecular forces are not well known, particularly at the high energies necessary to chemical reactions, calculations could only be suggestive and would not lead to quantitative agreement with experiments.
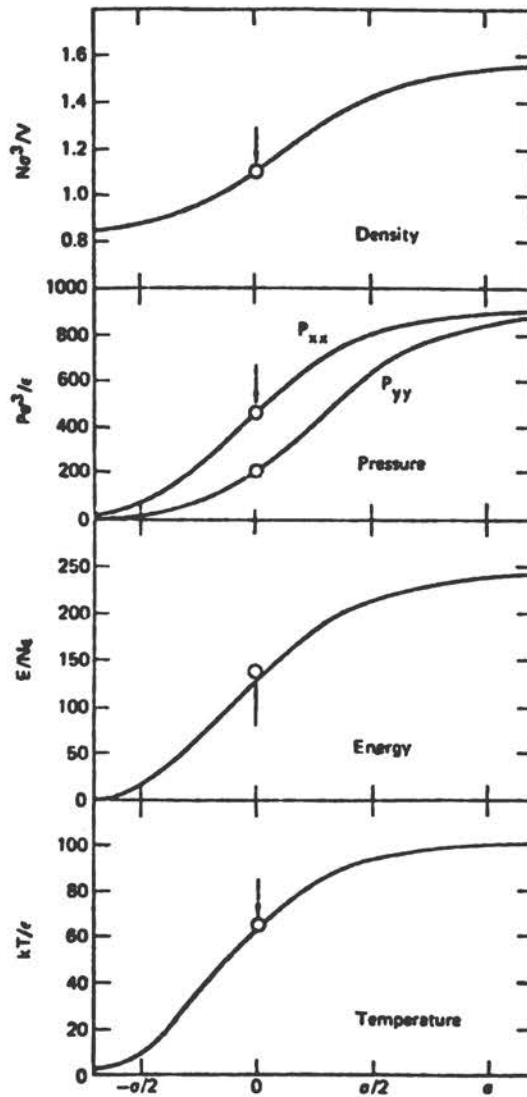
FIGURE 5-1.   Density, stress, energy, and temperature profiles from
the Navier-Stokes equations. The circles indicate
values from the molecular dynamics simulation. The
agreement for density and P_{xx} is assured by mass and
momentum conservation. The conditions correspond to a
40-GPa shock wave in liquid argon with σ = 0.3 nm and
ϵ/k = 120 degrees Kelvin. [Hoover et al., 1980]

P_{xx} =   pressure in the direction of shock
                  propagation.
ϵ =   depth of Lennard-Jones potential
k   =   Boltzmann constant
J   =   "collision" separation of argon atoms: i.e.,
                  point at which potential = 0
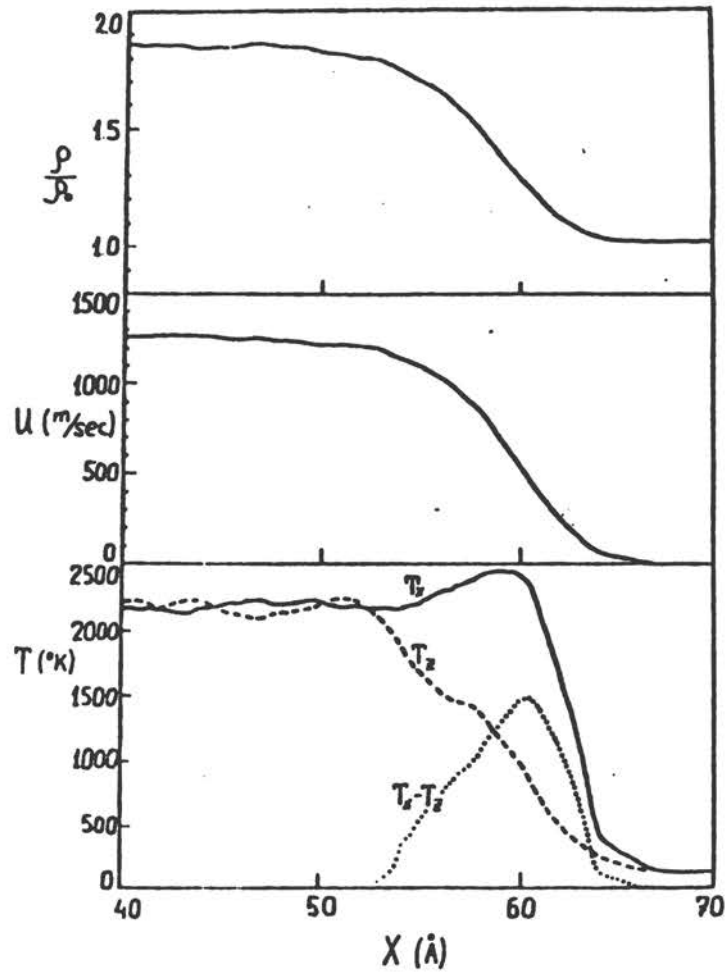
FIGURE 5-2. Density, particle velocity, and temperature
components T_x, T_z for shock wave ($u = 1250$ m/s,
$D = 2650 \pm 50$ m/s, $P = 30.5 \pm 0.6$ kbar) in liquid
argon ($\rho_0 = 0.92$ g/cm^3, $T_0 = 148$ K) [Dremin and
Klimenko, 1979].

u	=	particle velocity
o	=	shock velocity
ρ_0, T_0	=	initial density and temperature

DISCUSSION

The processes of principal interest are those that occur as the shock passes over a molecule of the material and those that occur during the quiet period behind the shock front, where pressure is more or less uniform except for changes resulting from chemical reactions. Later occurrences, during unloading and during the time that elapses between unloading and examination of the sample, are also important, but they fall more nearly into the province of known processes than do the others.

The shock front is hard to define precisely. The working definition among molecular dynamicists and those who study shock waves in gases relates to the region of equilibration of translational motions, leaving the equilibration of rotation, vibration, defect structure, chemical reactions, diffusion, etc., to the quiet period of more or less uniform pressure. It is then reasonably well established on theoretical and numerical grounds that shock thickness in an ideal lattice or in a homogeneous fluid does not exceed a few interatomic distances. This knowledge or belief does not translate easily into shock thickness in a real solid, including large molecules, defects, grain boundaries, impurities, etc., or in a porous solid or loose powder. We need to develop a clear and pragmatic description of the shock front in the real materials that are used in experiments.

Given that we have been able to suitably describe a shock front, we must examine the events that occur while the shock passes a point in the material. The initial effect is deformation of the mean potential well in which an atom is vibrating. Neighboring atoms will experience the same or similar deformation, but for a short time there is an asymmetry introduced that causes one atom to be accelerated and abnormally displaced relative to its neighbors. The acceleration has increased the vibrational energy of the molecule in which it resides. If the molecule is large, it may have been abnormally deformed. When defects are present, they represent a perturbation in the potential that may extend over many lattice spacings. The result of shock passage may cause major momentary deformations of such perturbations. Atoms of different masses will normally be expected to experience different relative accelerations.

It is evident without calculation that we can expect perturbations in the vibrational states of a molecule and that there is potential for significant change in the defect structure of a solid. What is less evident is that the electronic states of molecules may be changed as a consequence of the deformation. When electronic states change, the chemistry is different, so there is in principal an opportunity for significant chemical changes in the shock front if the shock front is thin relative to the constituent molecules. This opportunity arises because atomic speeds are less than shock speeds and electronic speeds are very much faster. Similar situations may exist around defects, even for small molecules.

What is evidently required to investigate these matters more thoroughly is to construct approximate models in order to develop concepts, to use these to guide molecular dynamics and quantum chemical calculations, and to probe the system using techniques that are sensitive to both electronic and vibrational states.

Molecular dynamic methods provide a model for numerical computations that work well as long as temperature is high and interactions among mass elements (molecules or atoms) of the system can be described by pair potentials. When interaction potentials are multiatomic and depend on the positions of many other atoms, as occurs within a molecule, present methods cannot be applied. It may be possible to combine molecular dynamics with quantum chemistry calculations to extend computations to some molecular systems, but this development lies in the future.

Experimental contributions to questions about processes in the shock front are limited and of mixed quality. Direct measurements of shock rise times in condensed materials normally give values the order of magnitude of 10^{-9} second or greater. Harris and Presles have described the results of optical refraction measurements in water that give a rise time of about 10^{-11} second [Harris and Presles, 1981]. There seems little doubt that, locally at least, the rise time is the order of a few atomic spacings in simple materials, insofar as translation is concerned. The effects of heterogeneities in the sample may make the apparent macroscopic thickness much larger.

A direct measurement of the pressure-induced Raman shift behind a 1.5-GPa shock in liquid benzene shows that the mode had reached equilibrium within not more than 1 microsecond of the shock front passage. This supports laser excitation studies that show that vibrational equilibrium is reached very quickly in large molecules.

The electronic spectroscopy being carried out at Washington State University shows extraordinarily large changes in absorption spectra, even for quite weak shocks [Ogilvie and Duvall, 1983]. At present it has a time resolution of about 30 nanoseconds. This can be readily increased to 1 nanosecond. It is certainly suitable for probing the region immediately behind the shock front. Improvements in resolution beyond 1 nanosecond are speculative at this time.

The attempts being made at the Naval Research Laboratory to develop a method for producing a shock wave by absorbing the output from a laser in a thin foil immersed in a fluid are interesting but fraught with difficulty. The intent is to synchronize shock production with a laser probe and thereby make it possible to use picosecond laser techniques to investigate phenomena in the shock front. Shocks have been and are being made by laser absorption. Obtaining the precision required to make the desired measurements will be difficult, but it should be encouraged because of the advance it would represent.

The production of defects in the shock front is fairly well confirmed by shock wave decay measurements, which attest to the need for dislocation generation in the front, and by electrical conductivity measurements in silver [Dick and Styris, 1975], which point to vacancy generation. Electrical polarization measurements also confirm defect generation to the extent that they are due to induced, not permanent, dipoles. Dislocations are also known to be generated in large numbers by plastic flow behind the shock front, so the presence of defects does not automatically imply generation in the shock front.

Abnormal mass diffusion resulting from differential acceleration of light atoms relative to heavy ones is suggested from time to time to explain various observations, such as diffusion of powders into metal surfaces or explosive welding phenomena. Experimental evidence is less than satisfactory, and it is hard to find a theoretical model for such motion, but the suggestion cannot be discarded out of hand [Zemsky, Ryabehikov, and Epshteyn, 1979; Batsanov, 1979].

One of the important uncertainities in shock experiments is temperature of the shocked state. Various attempts have been made to make dynamic measurements in the past, but those developed are mostly radiation-based and are not suitable for present purposes. The problem is particularly difficult and important in powders where temperature distribution is so heterogeneous.

Recent work in exo-emission from freshly fractured surfaces has shown that electrons, ions, and photons can all be expelled from such surfaces and that very large inhomogeneous electric fields exist on such surfaces if they are insulators [Dickinson, Jensen, and Jahan-Latibari, 1984]. The potential for such occurrences in shocked insulators is very great, at least at some stage of the fracture process [Mineev and Ivanov, 1976]. And in metals it is expected that electrons in large numbers are emitted from severely strained metal surfaces. Moreover, very large temperatures have been measured at the tips of traveling cracks in insulators, a condition that could well lead to important chemical changes [Fuller, Fox, and Field, 1975; Weichert and Schonert, 1978].

These comments apply principally to single-shock loading of materials. Stepwise loading is a more complicated matter, and existing dynamic experiments do not yet shed much light on the processes that occur. However, it is worth noting that the spectroscopic experiment shown in Figure 1-2 does involve SW loading, and the spectral changes that occur during the loading process can be followed step by step for the first few steps and continuously thereafter. Moreover, the total band edge shift from SW loading is greater than that obtained with DIC loading over a 340-nanosecond interval, even though the time to reach maximum pressure in SW loading was of the same magnitude.

RECOMMENDATIONS

While the motivation for these studies has been scientific, direction
has been provided by potential applications. If such studies are
successful, the path to understanding prospects and evaluating technical
promise will be greatly shortened. It is in this context that the
following recommendations are offered.

Efforts to probe the uniform pressure state behind the shock front
using diagnostic methods that are sensitive to electronic and vibrational
states--i.e., electronic and vibrational spectroscopy--should be
continued.

Efforts to introduce picosecond laser techniques into the
investigation of fundamental processes in the shock front should be
continued, using care to ensure that the system being studied is
well-defined.

Quantum chemistry calculations tailored to address conditions thought
to exist in the shock front should be initiated. These should be coupled
with molecular dynamic and analytical modeling, with the aim of
determining molecular interactions and intramolecular motions within and
behind the shock front.

The development of semi-empirical theoretical descriptions of the
shock process, like that given by Klimenko and Dremin [Dremin and
Klimenko, 1981] should be encouraged.

The perturbation of fields around defect states produced in the shock
front should be examined, and the possible effects of such perturbations
on local atomic distributions and electronic states should be considered.

In situ methods for measuring temperature in shock waves should be
developed.

In following these recommendations it should be kept in mind that
monatomic fluids, polyatomic fluids, and solids require qualitatively
different models, and that one studies such models in order to develop
important concepts for guiding calculations and experiments.

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