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TITLE: FREE-EXPANSION EXPERIMENTS AND MODELING IN DETONATION: CHEMISTRY AND HYDRODYNAMICS ON A LABORATORY SCALE

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FREE-EXPANSION EXPERIMENTS AND MODELING IN DETONATION: CHEMISTRY AND HYDRODYNAMICS ON A LABORATORY SCALE

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Laboratory-scale (25-50 mg) detonations of PETN, RDX, HNS, and TNT have been carried out in a high-vacuum chamber, and collisionless molecular beams of the freely expanding detonation products have been analyzed as a function of time with a mass spectrometer. Concurrently, time-sequenced schlieren and shadowgraph images of the initial expansion of the product plume are recorded using a pulsed laser for illumination. These data tie the chemistry and hydrodynamics of the detonation event together. The results, interpreted with the aid of a computer model, suggest that this experiment freezes the chemical reactions of detonation by rapid adiabatic cooling and provides a continuum of samples in the molecular beam, representing the sequence of reactions in the detonating charge. With a suitable model of the expansion hydrodynamics, the hydrodynamic histories of a sequence of volume elements can be associated with their frozen chemistries. We expect experiments like this to provide a test for molecular models of detonation.

INTRODUCTION

Chemical reactions drive detonation through several measurable processes. Among these are shock (hot-spot) initiation, run-to-detonation, reaction zone chemistry, and reactions during product expansion. Insofar as these processes are measurable, they deviate from the assumption of instant equilibrium and affect the process of detonation. Yet, we know almost no details of these important chemical processes, which, with hydrodynamics, form the basis of detonation science and engineering. Although molecular quantum mechanics is making contributions to low-pressure combustion science, it does not assist effectively in understanding detonation because the molecular detail necessary to test and challenge theory under detonation conditions (up to 10^6 atm and 5000 K) is lacking from detonation experiments. The work we describe here provides a look at detonation processes in the molecular detail necessary to link molecular quantum mechanics to detonation science. Further development and modeling of these experiments appear to have potential as a laboratory-scale test for high explosives that simultaneously measures several aspects of sensitivity, performance, and chemistry. Numerous publications of this work have already appeared.[1-6] This paper will be an overview of the main features of the progress made to date.

EXPERIMENTAL RESULTS AND DISCUSSION

We have reported some experimental data identifying the major reaction products of some common solid explosives, such as HNS,[1] PETN,[4] and RDX.[5] Here we report additional data on these explosives and new data on TNT. Almost all of the studies were conducted with laboratory-scale explosive charges of 25-50 mg, and all were reasonably "pure" detonator-grade explosives without plastic binders. They were detonated in a vacuum chamber using only slappers, except for TNT, which required a PETN booster charge of about 10 mg. The apparatus used to make the measurements has been described previously in some detail,[1,4] but briefly can be described as a vacuum chamber with dimensions and operating conditions that permit the free expansion of the detonation products to occur without any collisions other than intermolecular collisions between the products themselves. That is, this method samples the detonation products without reshock. A skimmer admits a collisionless molecular beam of the expanding products to a mass spectrometer where the abundance of a chosen molecular mass is measured as a function of time. By interpreting our experimental data with computer models, we find that some of the products we observe represent conditions that occurred less than a fraction of a microsecond after the detonation wave passed through the explosive charge. For some explosives such as TNT and HNS, these products are probably characteristic of the reaction zone conditions.

Figure 1 shows composite time-integrated spectra from the explosives PETN, RDX, HNS, and TNT. The most striking characteristic of these spectra is that, in all four cases, they differ enormously from the spectra expected from complete reaction of the explosive. For example, Figure 2 shows the reconstructed spectra of the products observed in a detonation calorimeter from these same explosives.[7] The calorimeter detonations were confined inside a gold pipe, so those products expanded slowly and are believed to represent typical detonation products quenched by freeze-out in the vicinity of 2300 K. On the other hand, the free-expansion spectra presented here show many more components and a markedly different distribution of the expected equilibrium products, H_2O, CO_2, CO, and H_2. A possible explanation is that the free expansions are much more rapid (see Modeling), freezing out a variety of reaction intermediates from incomplete reactions. These intermediates might be stable molecules or even free radicals. It is startling to note that the explosives appear to detonate, but the products observed are not the expected final products. If this is true, a process closely resembling detonation can occur without the expected complete reaction! Mechanisms of detonation at the molecular level will have to take into account results like these.

Other comparisons are also interesting. HNS and TNT are oxygen-poor explosives that produce lots

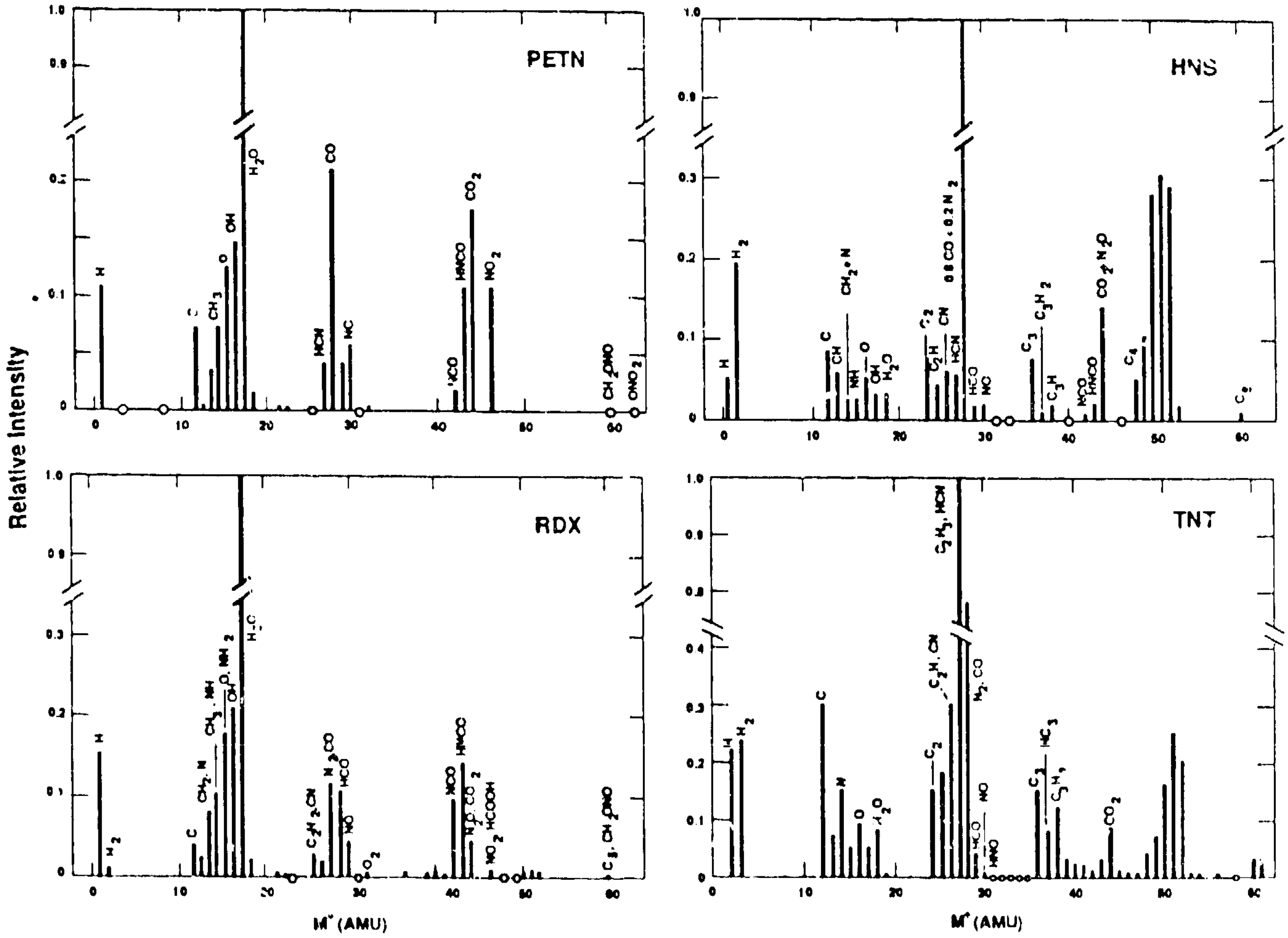

FIGURE 1. THE TIME-INTEGRATED SPECTRUM FROM THE FREELY EXPANDING DETONATION PRODUCTS OF PETN, RDX, HNS, AND TNT. IN EACH SPECTRUM MASS PEAKS ARE LABELLED WITH POSSIBLE PARENT OR FRAGMENT IONS. THESE SPECTRA FROM RAPIDLY QUENCHED DETONATIONS CAN BE COMPARED TO THOSE EXPECTED FROM SLOWLY QUENCHED DETONATIONS SHOWN IN FIGURE 2.

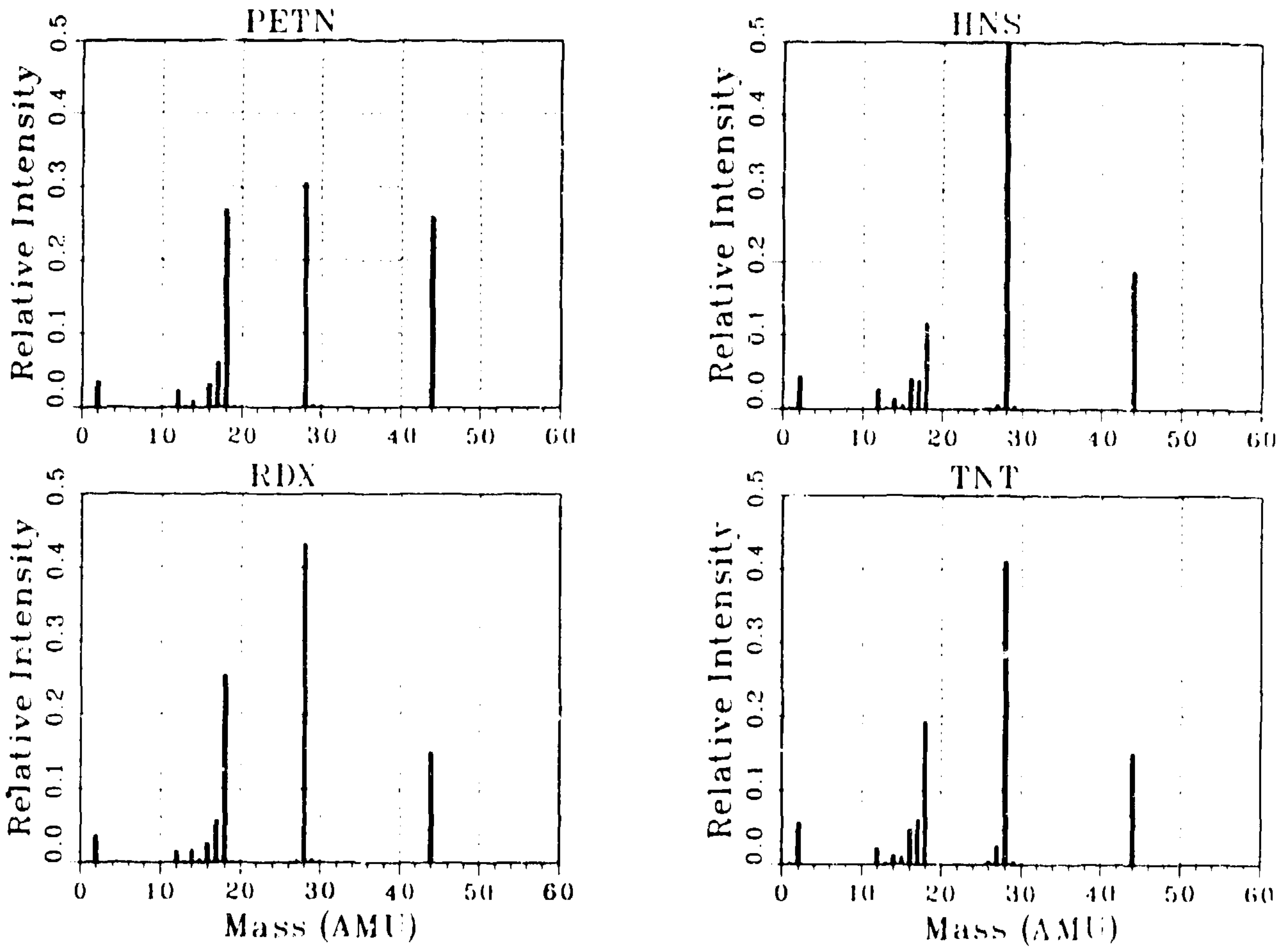

FIGURE 2. RECONSTRUCTED SPECTRA OF THE DETONATION PRODUCTS OBSERVED FROM SLOW QUENCHING IN A DETONATION CALORIMETER.[7] THE PRODUCTS ARE APPROXIMATELY THE DISTRIBUTION EXPECTED FROM THE BKW EQUATION OF STATE AND A FREEZE-OUT TEMPERATURE OF 2000-2500 K.

of soot in the products,[7,8] whereas PETN and RDX have a higher oxygen balance. It is evident that the oxygen-poor explosives have spectra that are similar to each other. Similarly, RDX and PETN have spectra that are much alike but differ considerably from the two oxygen-poor explosives. There were no significant product intensities at masses larger than 60 mass units, where some effort was made to find larger clusters of soot or mass peaks of unburned explosives.

We are also examining the effects of charge size on the intensity of the product distribution. Preliminary results indicate that, for a material like PETN, the product spectrum does not change over the range of sizes studied, as long as a clear indication of detonation is present. For other explosives, presumably with more extended reaction zones, we see evidence of charge-size effects. These studies are still in progress.

Time-resolved schlieren and shadowgraph images of the first 35 mm of the detonation product expansion have been recorded for several of the explosives. These data give a useful view of the initial stages of the expansion dynamics, such as profiles of expansion-front velocity and density, which can be compared with schlieren images derived from our computer model described below.[3,9] These time resolved images are closely related to the product equation of state, the detonation velocity, and the progression of the detonation front through the explosive pellet. Some information about slow chemical processes, such as soot formation, may be obtainable by comparing simultaneous schlieren and shadowgraph images of the expanding charge.

MODELING

A common question is whether the small charges we study, particularly of the less sensitive explosives, are really detonating. The schlieren and shadowgraph photography and the modeling of the early expansion now give us independent information to assess whether they are detonating or not. The images for PETN, RDX, and HNS indicate that the early rapid acceleration of the products, the product velocities, and the product density profiles are as expected from detonations, and the experimental images agree with images computed with the KIVA code using the equation of state (BKW) of the expected detonation products.[3] The expansion-front velocity profiles computed by KIVA also match the velocities observed experimentally. Under free-expansion conditions, the expansion front is expected to have a velocity equal to the local particle velocity plus the sound velocity in the medium if gamma is equal to 3, as it is, approximately, for many explosives of interest. The expansion front velocity under these conditions is also equal to the detonation velocity, a fundamental performance parameter for an explosive. Further work on this result is being done to extend this concept to conditions where gamma may differ from 3.

The molecular density as a function of arrival time measured at the mass filter also agrees quite well in several respects with KIVA computations. A density-vs-time curve is recorded for each mass, then a time-resolved spectrum is obtained by plotting density-vs-mass for each 10 µs time interval (Figures 3 and 4). The composition recorded for each 10-µs time period corresponds to a particular volume element on the axis of the charge, identifiable by the hydrodynamic model and the equation of state used in the KIVA calculation. A mass spectrum of the material coming from each volume element can then be constructed by assembling the mass filter data for the corresponding time period from individual shots with the filter tuned for each mass in the spectrum. A hydrodynamic history (density, temperature, and other properties vs time, Figure 5) can be computed for each volume element sampled (approximately 0.02 mm in the charge corresponds to the 10-µs sampling time at the mass spectrometer) so that the time-sequenced chemical analyses associated with that volume element can be interpreted kinetically. The chemical data (Figures 3 and 4) can then be used to test reaction mechanisms and rate parameters derived from quantum mechanical reaction dynamics calculations.

Another process under investigation is solid-phase carbon formation. The Shaw-Johnson (SJ) diffusion model[10] can be incorporated into KIVA to give estimates of the progress of that process as a function of time and position in the charge. The schlieren and shadowgraph images recorded for HNS detonations appear to give evidence for solid particle formation early in the product expansion. After a small amount of expansion, PETN and RDX become and remain transparent to the laser light used to record the shadowgraph images, but, in the case of HNS, within about a microsecond the product plume again becomes opaque, suggesting the formation of light-scattering material in the products. The KIVA code is being modified to compute particle-growth kinetics from the SJ model and light scattering by the resulting particles for comparison with the time sequenced experimental images.

In addition to the interpretation of experimental results, the modeling with KIVA is being used to refine experimental configurations and to design improved apparatus and instrumentation.

CONCLUSIONS

These results are revealing the details of a new chemical dimension in detonation science. Experiments with real, not surrogate, explosives are providing provocative new data on the basic chemical processes underlying sensitivity and reactivity in high explosives. It is expected that this database will provide a robust test for molecular quantum mechanical models of bonding and reaction dynamics in explosives. Additionally, these experiments hold promise for elucidating the interaction of chemical and physical effects, such as in the tribochemical processes believed to be the basis of hot-spot initiation of detonation by shock and impact. Finally, these experiments and the associated modeling appear to give us a prototype laboratory-scale test that links quenched detonation chemistry with shock sensitivity and a rudimentary measure of detonation performance.

ACKNOWLEDGMENTS

Peter O'Rourke and Tony Amsden assisted greatly in adapting the KIVA code for this work. Jim Ritchie provided BKW calculations. Scott Murray assisted in making the mass spectra data base, running the KIVA code, and interpreting the output. Wilbur Fernandez assisted in running the experiments and in maintaining and modifying the apparatus. Discussions with Wildon Fickett and Jack Jacobson concerning modeling of detonation have been most helpful.

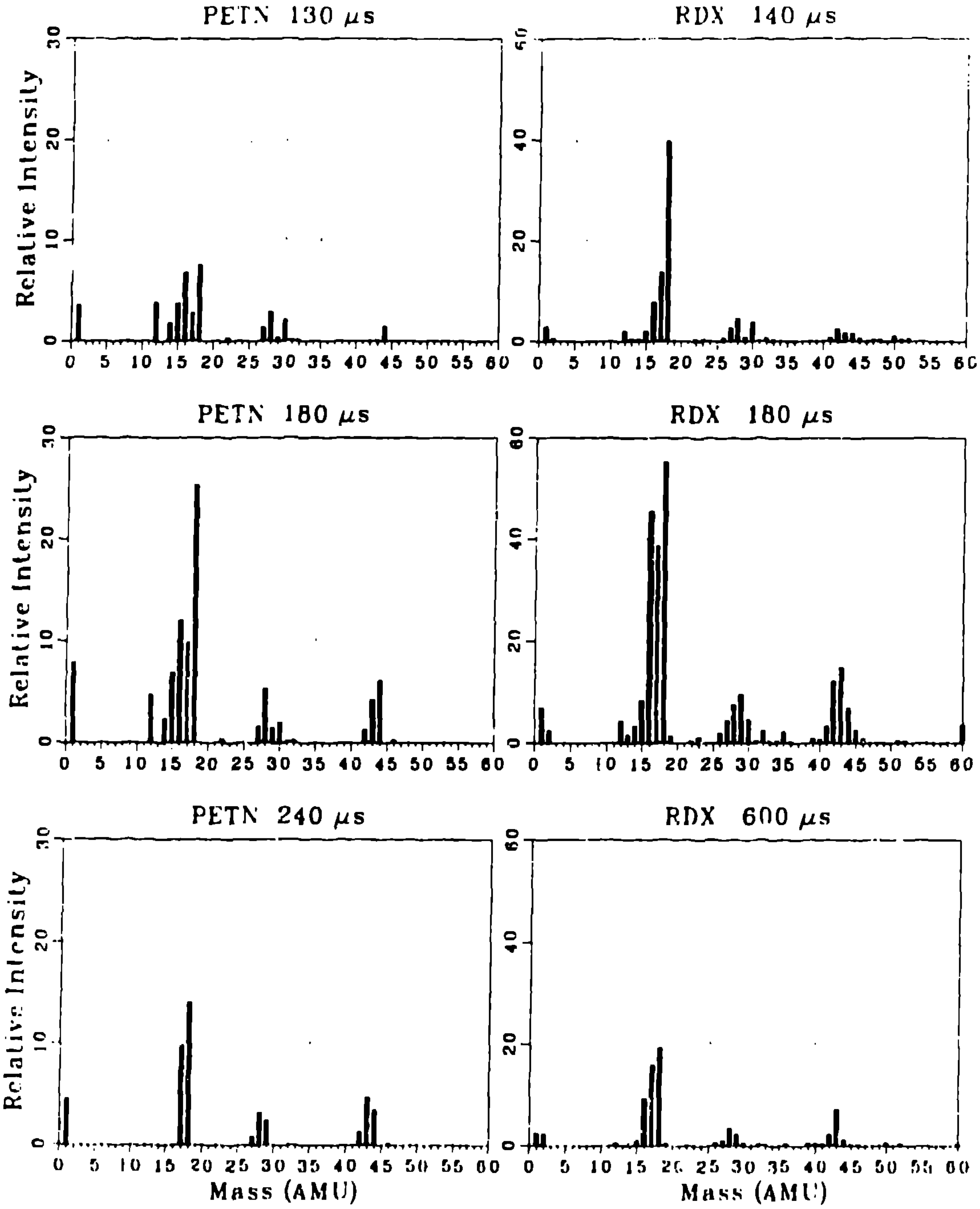

FIGURE 3 TIME-RESOLVED SPECTRA OF THE EXPANDING PRODUCTS FROM THE DETONATION OF PETN AND RDX IN A HIGH VACUUM. FOR EXAMPLE, WITH PETN THE INDICATED TIMES OF ARRIVAL AT THE MASS SPECTROMETER CAN BE MAPPED APPROXIMATELY TO CORRESPONDING DEPTHS IN THE INITIAL CHARGE (MEASURED FROM THE CHARGE SURFACE NEAREST THE SPECTROMETER) AS FOLLOWS: 130 μS (0.04 MM), 180 μS (0.10 MM), AND 240 μS (0.20 MM). THE 10-μS TIME RESOLUTION OF THE MASS SPECTRA CORRESPONDS TO 0.02 MM IN THE CHARGE, AND THIS NUMBER DIVIDED BY THE DETONATION VELOCITY OF 8 MM/μS GIVES A TIME RESOLUTION OF 2.5 NS IN THE DETONATING CHARGE. THE PETN PRODUCT WAVE ARRIVING AT THE MASS SPECTROM-ETER PEAKS AT 165 μS AND THAT OF RDX AT 200 μS. THESE PEAKING TIMES ARE SHORTER THAN THOSE OF HNS AND TNT IN FIGURE 4.

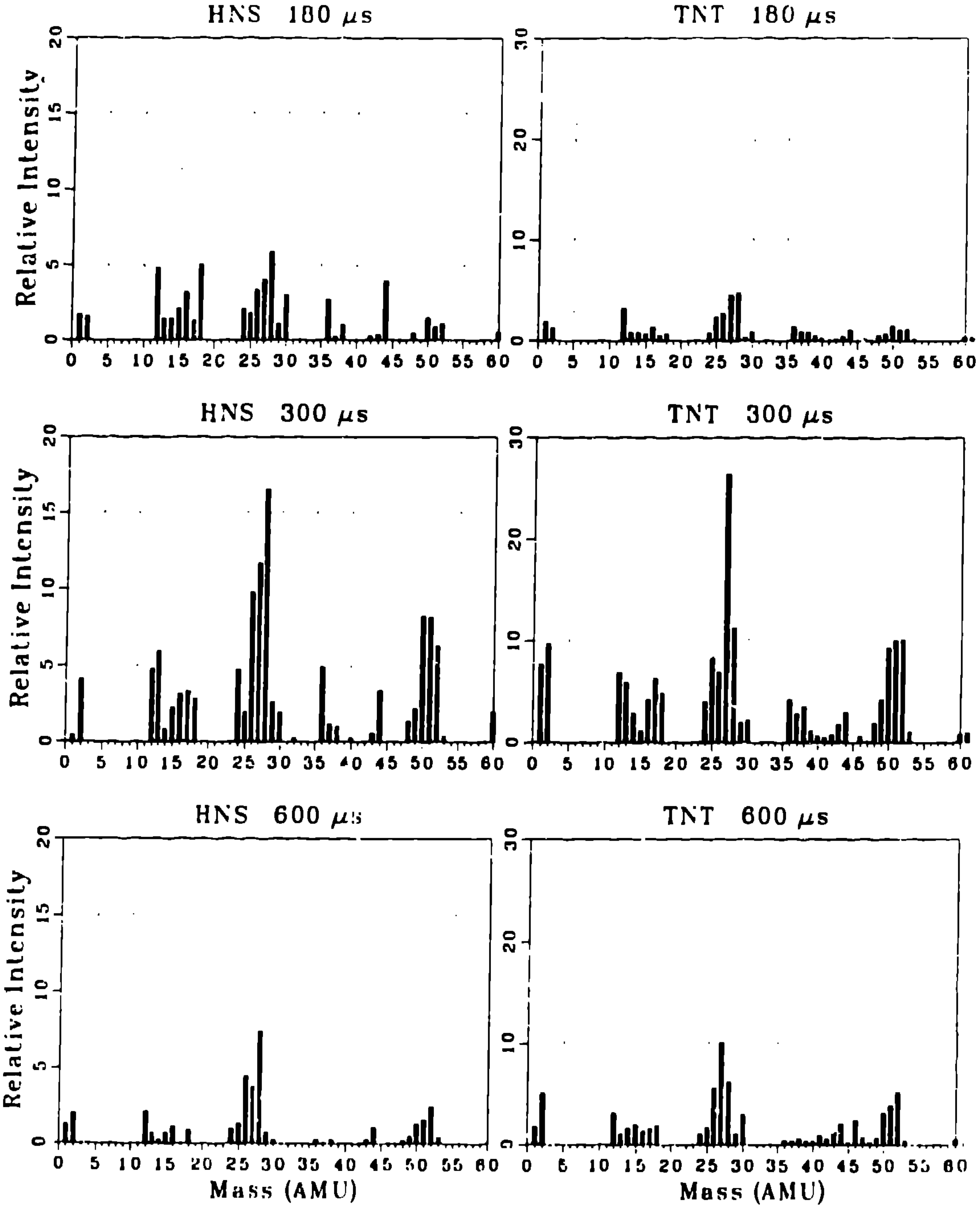

FIGURE 4. TIME-RESOLVED SPECTRA OF THE EXPANDING PRODUCTS FROM THE DETONATION OF HNS AND TNT IN A HIGH VACUUM. THE ARRIVAL TIME OF THE PEAK FOR THE PRODUCTS FROM HNS IS 300 μS, AND THAT OF TNT IS 325 μS.

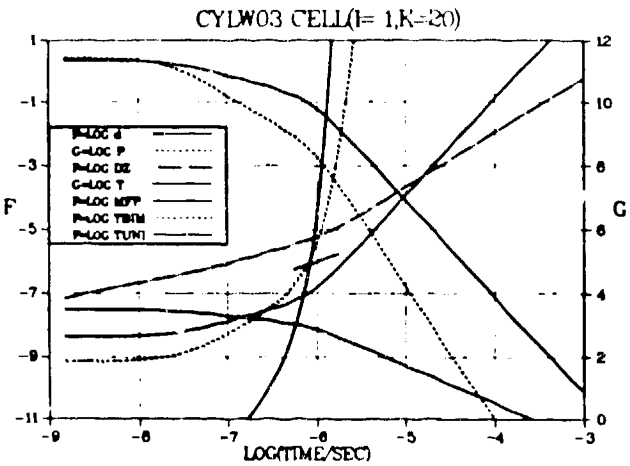

FIGURE 5. HYDRODYNAMIC HISTORY CALCULATED BY KIVA FOR CELL (1,20) OF A 3-MM-DIAM X 3-MM-HIGH CHARGE OF PETN WITH AN INITIAL DENSITY OF 1.67 G CM^{-3}. THIS CELL IS ON THE CHARGE-SKIMMER AXIS AND IS THE FIRST LAYER (0.15 MM THICK) TO EXPAND INTO THE VACUUM. UNITS OF THE PARAMETERS ARE CM-G-SEC-K UNITS. D = DENSITY, P = PRESSURE, DZ = MEAN DIFFUSION DISTANCE, T = TEMPERATURE, MFP = MEAN FREE PATH, TBIM = REACTION TIME FOR A BIMOLECULAR REACTION (A = 10^{12} CM^{3} MOL^{-1} S^{-1} AND E = 10 000 CAL MOL^{-1}), TUNI = REACTION TIME FOR A UNIMOLECULAR REACTION (A = 10^{16} S^{-1} AND E = 40 000 CAL MOL^{-1}). THE PARTIAL LINE CUTTING THE LAST TWO CURVES INDICATES THE POINT OF QUENCHING.

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