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USING LABORATORY SCALE SAMPLES

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DETONATION CHEMISTRY STUDIES OF ENERGETIC MATERIALS USING LABORATORY SCALE SAMPLES

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ABSTRACT. We describe an apparatus by which the detonation products of an explosive can be identified and whose relative concentrations can be determined quantitatively. These measurements can be made on products that have been formed in less than one microsecond after the passage of the detonation wave. The technique is based on the rapid quenching of chemical reactions by virtue of the free expansion of the products into vacuum. Of course, products that have been formed over a longer period of time and under different pressure/temperature conditions can also be studied. Time resolved molecular-beam mass spectrometry is used, so that whether detonation occurred or not in forming the products can be determined. We describe optical techniques, principally Schlieren photographs, that also confirm detonation. We report measurements made on six standard explosives, PETN, RDX, HMX, HNS, TNT and TATB, and one research explosive, nitric oxide. For none of the standard explosives do we measure product distributions that agree with model predictions based on equilibrium assumptions. A computer model of the free expansion is described briefly and its importance to the interpretation of the data is emphasized.

INTRODUCTION

The apparatus that I am going to describe and the experiments performed thereon are intended to provide, in the long term, data that lead to the identification of the important chemical reaction

mechanisms or pathways that are responsible for the propagation of detonation waves in explosive materials. The convening of this conference is evidence that this is an important goal to some people, at least. But we know that this chemistry remains, in large part, a mysterious process except that in very general terms it is an oxidation process or a "flame" initiated by a shock.¹ In my view, the mystery arises because the chemistry involves reactions that are a direct consequence of what are now called "many-body interactions," a subject that is not well understood and which only now is being tentatively probed by chemists. Because it is a relatively new subject, it promises to be an exciting time for some of us.

In the shorter term, as a necessary step to studying the chemistry of detonations, we want to know what the products of those chemical reactions are. We already know the identity of the reagents in detail, because analytical and crystal structure fields are well established disciplines and have long been applied in explosive studies. But the reaction products are not so easy to identify. The equilibrium products can be inferred from thermodynamic considerations, and very careful measurements have confirmed that these are the products one finds some time after the Chapman-Jouget (CJ) conditions have been attained.² For many applications, this is all the information that one needs. Very successful models of the detonation wave propagation in specific explosives are being developed using only the heats of formation of the explosives and their bulk physical properties. These successes don't provide much insight into the chemistry that drives the process, however, because their successes seem to be insensitive to any input about chemistry. As a kineticist, I am impressed by the hydrodynamic models and shock wave measurements, but I very much would like to know what the products of the reaction are in the region between the CJ point and the detonation front, and their relative concentrations. We know of no experiments that have provided information of this kind for any explosive, although one or two molecular species have been identified spectroscopically.³ In the following presentation, we will describe an apparatus and some

experiments which we feel attain the goal of providing the desired reaction product spectrum.

EXPERIMENTAL ARRANGEMENT

The idea behind our experimental arrangement is to take advantage of the rapid cooling of the detonation products that occurs if these products are allowed to expand freely without impediment to the stage where they become isolated molecules. So the apparatus is designed to be able to look at those reaction products for which the expansion and the subsequent cooling is maximized, the free surface at which the detonation wave ends.

We use small, generally cylindrically shaped explosive charges having a mass of about 20 mg to 100 mg in weight. The charges are shocked to detonation from one end of the cylinder so that the detonation wave ends at the other end of the cylinder. The material at this far end subsequently expands away from the body of the now hot, still very dense products of detonation, with a velocity close to that of the detonation wave. The expansion is sufficiently rapid that the effective temperature of those products is reduced to the point that chemical reactions are quenched in a time that we calculate is less than a microsecond. This time, then, determines the time duration between the passage of the detonation wave and our ability to examine the product concentrations. For some explosives, such as TNT, our data suggests that some of the products are from that region of detonation wave propagation called the "reaction zone." During our experiments, the time over which measurements are made is considerably longer than one microsecond, but these times are not relevant except for those products that can change their states spontaneously, for example by radiation.

Our "work-horse" method of identifying the reaction products is electron impact ionization mass spectrometry. We feel that this method is one of the most generally universal for all chemical species and sufficiently adaptable for fast measurements to be the central focus in the instrument design. It is now a well developed technique developed by chemical kineticists during the

1970s that is ideal to examine those detonation products at the leading edge of the expanding gases, that of molecular beam mass spectroscopy. By the time that the gases have expanded to about ten times the original pellet dimensions, the temperature is low enough that there are scarcely any collisions at all. Thus the molecules are now moving in unison, and we can utilize molecular beam forming techniques to direct them into a mass spectrometer designed especially for molecular beam detection. This allows us to obtain a mass spectrum of the products that reflect directly the concentrations they had at the time that the expansion quenched the reactions that formed them. Moreover, by allowing the molecules to drift, collisionlessly, over a measured path length we can measure their velocities with reasonable accuracy and obtain a time history of the density of a product in the expanding gases.

Figure 1 is a diagram of the apparatus we use which has the characteristics to do what we have described above. It consists of three principal parts: the detonation vacuum chamber, the molecular beam skimmer and differential pumping chambers, and the quadrupole mass spectrometer detector.

The detonator vacuum chamber is large compared to the other parts of the apparatus, and contains the apparatus to detonate the charges and sometimes optical components for spectroscopic studies. Its dimensions are determined by several considerations, the first being that the pressure rise that occurs in it following the detonation of the explosive charge does not adversely affect the other parts of the apparatus. Having a volume of about 280l, detonating a 100-mg charge gives rise to a pressure increase of about 100-200 mPa (1-2 micron). But in determining its dimensions it is also important to consider that no surfaces are located in a position to intersect and reflect molecules back into the drift region of the molecules to be formed into the molecular beam. These considerations also determine where we locate a rotatable carousel that supports and aligns the detonator stations. We can fire a charge every 5 minutes, which is the time that we normally need after each shot to evacuate the chamber to a pressure of 10^{-4} Pa (10^{-6} torr). At these pressures, the mean free path for

collisions in the ambient gas is several meters, so that the detonation product expansion is a "free expansion".

The skimmer serves the function of forming a molecular beam of those products that we want to examine under the collision-free conditions we discussed above. Its design is somewhat critical because the density of the gases are high when they arrive at the skimmer. If many molecules collide with the edges of the skimmer aperture, they can be reflected back into the oncoming particles that follow in time and cause a shock to be formed that distorts the velocity and temperature of the beam. Our skimmer is designed to minimize these types of collisions by virtue of a very sharp cone angle (15 degrees) and a very thin edge (1/40 mm).⁴ The skimmer aperture is 1 mm, and we estimate that about 1% of the molecules that are intercepted by the skimmer are scattered back into the path of oncoming molecules. Two stages of differential pumping follow the skimmer that serve to effectively isolate the mass spectrometer detector from the large pressure variations of the detonation chamber.

We detect the molecular beam with a quadrupole mass spectrometer.⁵ The combination electron impact ionizer-mass filter-electron multiplier is estimated to have an overall efficiency of detection between 10^{-7} and 10^{-8} for a nozzle beam of argon atoms. The vacuum chamber in which it is housed never rises in pressure above 10^{-7} Pa (10^{-9} torr), and a cryopump is located so that any neutral molecules that escape the detector are trapped in the cryopump. Except for very low mass signals, all of the detonation signals are very large compared to background. Pulse counting electronic signal processing is used in conjunction with a multichannel scaler (MCS) so that a time history of the product density arriving at the detector is obtained as standard data. Time of flight velocity analysis is routine over the 110 cm drift path taken by the products from the detonation point to the ionizer. Actually an apparatus preceded ours with design characteristics that were very similar in many respects⁶ but our apparatus was developed independently. A mass spectrum of PETN, one of the

explosives we will discuss here, was reported. However, no other work has appeared subsequently.

Figure 2 shows an example of the way our data looks from the molecular beam detector. The number of counts recorded in each channel of the MCS is plotted as a function of the arrival time at the detector. For convenience we have converted the ordinate from the channel number to the time elapsed to reach the center of each channel. Each channel is proportional to the number density of product molecules with the indicated mass at the indicated time after the explosive charge was detonated. The data shown is from PETN and the ion masses are for $M=15$ and $M=44$, the latter being scaled by a factor of 0.4. Since it is unlikely that $M=15$ is a fragment of $M=44$, the figure serves to emphasize that the threshold for the arrival of products at the detector is independent of mass, so that the higher mass has about three times the energy of the lighter mass. To show that the time history of the arrival of products at the detector contains information about the chemistry, in Fig. 3 we show times-of-arrival averaged over all of the masses for two explosives, RDX and TNT. They are clearly much different from each other, and we are tempted to speculate that the difference at the shorter times arises because of the difference in the length of the reaction zones of the two explosives. TNT has a longer reaction zone than does RDX, and thus some of the products originate deeper in the TNT pellet than it does for RDX and so arrives later at the detector. Unfortunately reaction zone data is not very common, especially for pure explosives we show here, and considerable differences of opinion exists about the meaning of their measurements. We point out that only one mass at a time can be examined for each detonation of a pellet of explosive. The reproducibility of the signal intensity for several trials at one mass depends very much on the particular explosive being studied, sensitivity and homogeneity apparently being important factors. For this reason, we always rely on at least six trials or more at masses with large signal intensities, and at least two or three for masses with little or negligible intensity. We are examining the use of time-of-flight mass spectrometers, and an ion-trap device to obtain the entire mass spectrum at one trial.

All of our explosive samples that we've used so far, with the exception of solid nitric oxide, contain 0.1 g or less. With NO, quantities of 25-35 mmole are used to ensure detonation. The densities are relatively low so that pure explosives can be detonated without booster charges. Kapton slappers driven by deposited copper bridges detonate all but the solid NO and TNT. For these, PETN booster charges are required.

A rotatable carousel allows us to load and fire up to 30 charges in the large detonation chamber without the need to vent the high vacuum for replacements. We can also use a carousel which has only 10 charges, but which can be cooled to 30 K to study explosives such as nitric oxide or to perform more exotic experiments some of which I will describe later.

COMPUTER MODELING

An indispensable part of the work connected with our program is the modeling of the detonation of the charges being studied and the subsequent free expansion of the detonation products. I will not discuss this aspect in detail in this lecture because the subject will be discussed by my coworker in another lecture. The interpretation of the data is very difficult without such modeling of the relevant events, and I will mention only a few points that bear directly on the experiments themselves.

A computer code called KIVA is being developed for the modeling process which can incorporate reaction kinetics during the gas phase portion of the expansion, after the detonation wave has reached the far surface of the pellet. Realistic equations of state of products are used, and the starting conditions include approximate conditions of a Taylor wave. The code has been used to simulate some of the optical diagnostics, such as Schlieren photography, that are a part of the experimental techniques we use. It accurately represents the leading edge velocity profile of the products as being closely the velocity of the detonation wave in the explosive material, and it predicts the density-vs-time profiles we observe experimentally. We use it to model the temperature distribution in the free expansion as a function of the stage of the

expansion, and it confirms that for some explosives, we should be able to distinguish products that originate in the reaction zone as the detonation arrives at the surface of the pellet in the field of view of the mass spectrometer detector. Figure 4 is a plot showing some of the relevant parameters that characterize the small volume near the surface of an explosive pellet. The temperature of the gas, the density, the pressure and the mean free path are included in this busy set of graphs, but I particularly want to call attention to the estimates of inverse of the rate constants for bimolecular exchange reactions and also for unimolecular process. A bimolecular reaction with an activation energy of 10 kcal/mole and an A factor of $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ is seen to reduce its rate a thousand fold and is effectively quenched in less than a microsecond after the detonation wave has reached the surface of that volume.

One of the assumptions of the code that we hope to examine in more detail is that there is very little mixing of the products that originate at different depths of the explosive charge during expansion. Preliminary studies have not yet refuted that assumption, but the experiments have not been very definitive on the mixing point. Should this assumption be borne out, then the model suggests that the time dependence of the arrival of each species in the products reflects directly the depth in the pellet at which the species was formed. Furthermore, the pressure and thermal history experienced by the products in each increment of depth in the pellet is also different, and calculations of the kind shown in Fig. 4 can be made for any distance from the pellet surface. Therefore, we should also pay attention to the experimental distribution of products for various time slices in a three dimensional plot of intensity as a function of mass and time-of-arrival.

ARE WE STUDYING DETONATION?

This question arises often enough that I am devoting at least a short section to its discussion. In my opinion the explosive charges for which we acquire data are detonating. It may be suggested that

this should not be a matter of opinion, but that we should be able to establish it unequivocally. Unfortunately, the matter is not that simple. The statement has been made that since a detonation is a steady state wave phenomenon, then a large amount of detonating material in an ideal geometry is necessary to ensure that a steady wave is established. Our sample sizes are sufficiently small that it becomes questionable if a steady wave forms for some explosives, especially for example in TATB where the reaction zone is measured to be of the order of the pellet size. With this strict definition of a detonation, there is perhaps some justification in the question. However, we have made various kinds of tests or measurements which indicate that our experimental conditions demonstrate some of the important characteristics of detonation. If ideal detonation is not occurring, then a high order process is occurring which has enough features in common with detonation to be of chemical interest to us. I discuss below some of the relevant test and measurements we look for to establish detonation.

Dent tests, or witness plate tests are made for each of the explosive materials that we study. We do this so that we can determine the slapper electrical energy, or the slapper size that is needed for the explosive pellet to reliably produce a dent larger in diameter than the pellet in a steel plate or rod held in contact with the pellet. Not only does this convince us that the pellet is detonating, but we are assured that we have minimized conditions that lead to variability we sometimes find in mass spectral intensity.

Schlieren and shadowgraph photographs are made of the freely expanding gases for most of the explosive materials that we've studied. The Schlieren images are particularly useful because we can make the sensitivity of the method high enough to locate the leading edge of the expanding products. With several photographs made at well timed intervals, the velocity of that leading edge can be determined with a simple ruler measurement. These measurements indicate that even in the early stages of expansion, within a few millimeters of the initial explosive surface, the velocity is approximately the detonation velocity. Our KIVA model

and other theoretical models⁷ indicate that this should be the case.

Time-of-flight measurements of the molecular products with the mass spectrometer are part of the data collection procedure, and velocity determinations are often made. Under conditions that have been determined by the dent tests and by Schlieren photographs to give detonation, the velocities of the early arriving products have velocities close to the detonation velocity of the explosive. This feature is very reliable, so reliable that if it is clear that the time history of the ion signal during a particular measurement does not have this high initial characteristic velocity, we assume that detonation was incomplete and discard the data. In just about every case that this happens there are other characteristics of the data that make it suspicious.

COMPARISON OF HYDRODYNAMIC DATA WITH THE MODEL

Figure 5 is a diagram of the optical arrangement that can simultaneously take a photograph in the Schlieren mode and in the shadowgraph mode, transverse to the direction of the expansion of the products. In the Schlieren mode, which effectively puts the image plane at infinity, a ray of light which is refracted by density gradients in the expanding gases by one milliradian or more is stopped by the aperture at the focus of the last concave telescope mirror. A dark region appears in the photographic image where that ray would have been in the absence of the refracting medium. On the other hand, the shadowgraph mode gives a different image for every finite image plane distance, and only at infinity does the Schlieren and shadowgraph look alike. In this mode we can look inside the dark regions of the Schlieren image.

Figure 6 is a set of slides of Schlieren and shadowgraph images taken with the apparatus of Fig. 5 with RDX. Each slide is a set of a Schlieren image and a shadowgraph image taken at the indicated delay after the detonator was triggered. Very striking to us is the highly directional characteristic of the expansion process seen most clearly in the Schlieren image. There is no resemblance to a hemispherical expanding cloud of gases that one might expect if one pictures the pellet explosion as being a conversion from a solid

to a high temperature, high density gas. One sees the remnants of the detonation wave in the shape of the pellet expansion. Also, there is a clear difference between the Schlieren and the shadowgraphs. The fact that the shadowgraph is looking inside the Schlieren image indicates that it is refraction arising from an index of refraction gradient that causes the difference in the images. The bright geometrical portions in the shadowgraphs are probably caused by lensing effects similar to the rings one sees on the bottom of pan of water if waves are set up.

If we do the same photography with PETN pellets, the images are much the same as for RDX. However the explosive TNT, HNS and TATB give very much different shadowgraph images from PETN or RDX. The shadowgraphs look so nearly as dark as the Schlieren images that they are indistinguishable. Evidently, the dark regions of the images do not arise from refraction for these three explosives, but from absorption of the light. As we will discuss later, carbon clusters are observed in the product distribution for these three explosives, and these clusters may be responsible for the absorption of light but we haven't established this yet. The only evidence we have to support the statement is that the shadowgraphs do not become completely opaque until one microsecond or so after the expansion starts, and large carbon clusters are relatively slow to form as compared to the production of other products.

A different slapper and support design was required to study the mass spectra of TATB and HMX, and we needed to use larger pellets. We found that the steering optics near the detonating pellets of the optical arrangement of Fig. 5 did not hold up for as many shots as were needed for a complete sequence of photographs. We were able to borrow a fast framing camera that took a sequence of 8 images that covered the complete range of the expansion⁸ with only one pellet firing. Figure 7, which is another slide, is a set of motion picture "stills" taken at one microsecond frame intervals with an illumination time per frame of 200 nanoseconds. Instead of a pulsed dye laser, the light source was an argon ion laser operating at about 1/2 watt of energy at 514.5 nm.

Firing an identical TATB pellet and detonator arrangement in air gives a much different expansion pattern than the one shown in Fig. 7. We show the effect that an ambient pressure of air at atmospheric pressure has in Fig. 8, which was also obtained using a fast framing camera.

MASS SPECTRUM OF DETONATION PRODUCTS

A composite plot of the mass spectra of six of the explosives that we have studied is shown in Fig. 9. For each of the explosives, the plots were obtained by summing up all of the counts in the channels of the MCS, up to channel 40,400 μ s after detonation of the pellet. The sum for each mass was then compared to that at a standard mass, several shots of which were always recorded for each run of from 17 to 26 shots. Thus provided with an intensity ratio, several instrumental variables were eliminated between runs made on different days. It is these ratios that we show in the plot, and, as we mentioned earlier each mass point is actually an average of several of these ratios. An adjustment is included in the plot to account for the mass transmission of the quadrupole mass filter, but no correction is made to the intensity for the ionization sensitivity of the electron bombardment ionizer. Thus the relative ion mass ratios of Fig. 9 are almost raw data of the mass spectrum. Making the more difficult corrections would necessitate having the identity of the parent molecule that gives ions at each mass. We have not progressed to that point yet. Truncating the sum at 400 μ s is arbitrary, but our intention is to eliminate from our analysis molecules that may appear at late times because they were directed into the detector by collisions with parts of the apparatus.

We estimate that the accuracies of the relative intensities shown in Fig. 9 are about 30%. Some of the more intense signals are perhaps more accurate than that with respect to each other, but we don't want to suggest that these spectra have the quality obtainable using refined analytical mass spectrometer instruments. For example, we do not obtain a good atom inventory for those explosives in the first column of Fig. 9, but we will discuss this more later. We intend these data to show important qualitative

features about the detonation products and how they compare to other information about them.

By comparing the two columns of Fig. 9, it is clear that there are at least two different classes of explosives represented. For PETN and for RDX, on the left, the mass 18 ion, which is almost certainly largely from H_2O , is the dominant product. Those explosives on the right, TNT, HNS and TATB, have the predominant intensities around mass 28 with very little mass 18 contributing to the spectrum. Mass 28 is a mixture of ions from CO and N_2 , and if we assign about a 20% N_2 -80% CO, the atom inventory from those spectra on the right are reasonably good. Mass 27, which is also fairly intense, must arise largely from HCN. We recognize that the right hand group consist of explosives which are considered to be oxygen poor, i.e., the ratio of oxygen to carbon is low for the formation of CO_2 . Those explosives on the left are oxygen balanced, with both RDX and HMX having almost identical chemical formulas. HMX, although it is placed in the left hand column, has a spectrum which has characteristics of both the oxygen balanced and the oxygen poor explosives. The mass 18 ion and the masses 27 and 28 are almost of equal intensity. Thus the expectation that its spectrum should look nearly the same as that of RDX because of its similar chemical formula is not borne out. The popularly used codes that calculate the detonation velocities, etc. of explosives at the CJ condition, such as BKW and Tiger, long have been known to require input parameters that can be grouped as RDX-like or TNT-like to reflect the fact that there are two groups of explosives based on relative oxygen content. Therefore our observations coming from Fig. 9 is not unexpected. What is unexpected is the way that this grouping manifests itself in the mass spectrum by the predominance of $M=18$ for one group and $M=27$ and 28 for the other.

There is no similarity between our observed product distribution and those predicted by the codes however. In Figs. 10 and 11 we have plotted several synthesized mass spectra obtained from experiments that quench the product distributions of detonations at near-equilibrium conditions at temperatures of about 1500 K to 2000 K.² Except for some differences arising because of a higher

temperature at the CJ point, these sorts of distributions are what the computer codes would also predict because they make the assumption of equilibrium between product states throughout the computations. To make the comparison to our mass spectra more appropriate, we have included the fragmentation pattern for the known products.⁹ For convenience, the figure also has our mass spectrum for the same explosive. It is clear that there are many differences between the equilibrium products distributions and those that we obtain. Conspicuously absent from the experimental results is a sizable intensity at $M=44$ coming from CO_2 or N_2O and an absence of a dominant product in the synthesized distribution. There is also evident a much richer distribution of products in the measured spectrum, and although some of ions are the result of electron impact dissociation in the ionizer, most of them have only a small fractional contribution from fragments of heavier parent molecules. Unfortunately we have not been able to reconstruct the neutral molecule product distribution that leads to the experimentally observed ion distribution.

All of the plots in Fig. 9 end at $M=60$. This is because we find no significant intensity above that mass. For each explosive, we searched at higher masses to convince ourselves that we hadn't missed an important product contribution. The mass at the molecular weight of the explosive molecule was always examined as well as masses below that value at which one would expect to see an ion if the parent explosive molecule were present in the products. What we found was that there were traces of ions at many of these masses, all the way down to the lower masses where the intensities rise for M less than 60. But it is difficult to do anything quantitatively with these traces of product, and we feel that their presence may account for the difficulty of getting a good atom inventory or mass balance from some of our spectra. From Fig. 10 it is clear that the measured spectrum of PETN has a lot of argon and nitrogen missing as compared to the synthesized spectrum. The problem of mass balance becomes much less acute for the explosives other than PETN and RDX.

In previously reported work,^{10,11} we've looked for comparisons with other types of studies related to explosives. Experimental studies such as thermal decomposition, laser irradiation decomposition (LIMA), impact induced decomposition, and even unimolecular decomposition have been examined to see if there is a common thread between decomposition and detonation products. Almost all of the products that we observe, which of course are gaseous, are in the list of products that some of these other experiments report. But quantitatively we don't find much in common, although that may be partly because not all of their products were reported in enough detail for a good comparison. Water seems to be especially difficult to measure in some of the methods and is only reported as being present. We conclude that the product distributions that we find, and which we are certain are closely related to the chemistry driving the detonation process, are not well represented by any other process at work in these other experiments.

Because we work on such a small scale, we can be somewhat venturesome in making measurements. I want to describe briefly some measurements of species that have not been reported in explosives by any other method, namely carbon clusters. The problem of soot formation is certainly a long standing one in any hydrocarbon combustion study as well as in modeling detonations. For example, neglecting the heat release from soot formation in BKW calculations of TNT can lead to serious errors,¹² sometimes even leading to the process being endoergic. In addition, the recent discoveries of small diamonds in the residue of contained explosions¹³ provides more encouragement to trying to understand the role of solid carbon in detonation products. The details of soot formation are still not well understood, but one of the mechanisms is thought to be an accretion process of atoms and small clusters to form clusters of increasing size as the process continues and the temperature of the product gases cool.¹⁴ So we examined the distribution of carbon cluster sizes under various conditions of detonation of HNS. In Fig. 12 we plot the relative intensities of products observed from HNS at the masses $M=12n$,

where n is an integer. We plot the intensities as if they represented the number densities of carbon clusters with n carbon atoms in each cluster. Up to $n=5$ were observable with our mass spectrometer, but we were expecting larger n values because we found HNS to leave copious quantities of solid carbon in the detonation chamber. We then repeated the cluster size intensity measurements while detonating the HNS under very different conditions. We cooled the detonator station holding the HNS pellets to a temperature of 30 K. A layer of solid Xe of about 20 to 30 mg was deposited by condensation on the pellet surface. This acts as a tamper to the surface layer of HNS about equal to half the thickness of the pellet to prevent its rapid initial expansion, and the intent was to see what the effect was of confinement. These results are also shown in Fig.12, and they are disappointing in that the resulting distribution is not really very different than the room temperature one. An equilibrium distribution of carbon clusters is also shown for comparison.

Evidently the products we examine from HNS at the early arriving times has not had sufficient time to accumulate many clusters to sizes much larger than $n=5$. We extended our search of carbon clusters to higher masses than $M=60$ for HNS also, even going as high as $M=720$ ($n=60$, the so-called Bucky-ball) without seeing large enough counts to distinguish from background.

OTHER EXPLOSIVE MATERIALS AND EXPERIMENTS

This section is a catch-all that I will use to describe work that we've done on unusual explosives and with techniques other than mass spectrometry.

We were able to shock solid nitric oxide with sufficient intensity that we observed the detonation products in our mass spectrometer.¹⁵ Fig 13 shows a sample of the data that we obtained with our cryocooled detonator-carousel upon which we vapor deposited nitric oxide to a solid. N_2 and O_2 mass peaks having all of the characteristics of velocity and intensity that we normally find for the usual detonation products of explosives were

seen, along with ions from the simple oxides of the material, namely NO, N_2O and NO_2 . These results confirmed what was inferred from equation-of-state measurements, that N_2 and O_2 were the principal products after detonating NO, and that some oxides of NO were also present. The oxides did not have quite the high velocities that N_2 and O_2 had, indicating that they were not formed as early in the process of the expansion of the product gases. For this particular study, the final atom inventory was quite good in that we were able to account for all of the atoms to within 5% with the suggested reaction mechanism. We also obtained an absorption spectrum of NO_2 from which we obtained an internal molecular temperature. This is the first time that we know of in which both a kinetic and a molecular temperature were measured for a detonation.

From a chemistry point of view, this reaction is very important because it exemplifies well the view expressed in the first paragraph of this article. That is to say that the intermolecular potential must be considered as having a many-body character to it. In gas phase, the reaction of NO that leads to the formation of N_2 and O_2 is known to proceed by an atomic mechanism, and requires temperatures of 4000 K to be measurable. At the densities and temperatures behind the shock that initiates liquid and also presumably solid NO, the concentrations of N and O atoms must be negligible. Therefore the reaction must occur in a concerted molecular fashion, and reactions of this kind have not been well studied so far. Simulations that we've done with very crude connections to the NO system indicate that if three or more molecules are involved, the concerted reactions between molecules become reasonably facile.

Experiments with isotopically labeled explosives can be done to good advantage with our apparatus. We hope to obtain some mass spectra with isotopically substituted constituents to resolve the indeterminacy of some of the mass peaks, such as $M=17,18$ and $M=27,28,44$. Deuterated PETN is available and we hope to obtain ^{15}N substituted TNT. But besides such standard uses, there are

other applications which are intriguing. Consider another application that we found which relies on isotopically substituted constituents. $^{15}\text{N}^{18}\text{O}$ was used in the NO studies to examine the question of mixing of products from various depths in the explosive charge. Layered deposits of solid NO were made with several alternating layers of normal NO and the isotopically substituted compound. We then examined the N_2 signal at masses 28, 29 and 30 to see if the time of arrival was representative of the layers that we had deposited. The results indicated that extensive mixing did not occur, but unfortunately they were not as definitive as we would have liked. We plan to repeat these kinds of measurements under different conditions.

As we mentioned earlier, spectroscopic methods have already been applied to identify and probe some of the species in the free expansion. We hope to expand on the use of optical methods with Transient Infrared Absorption (TRISP)¹⁶ and laser induced fluorescence. Because the CJ temperatures are only 2000-3000 K, most of the molecular products are in the ground electronic state. Emission spectroscopy looks selectively at only a few extraordinary molecules which are scarcely representative of most of the products. Infrared absorption, on the other hand is ideal for probing the vibrotational states of the ground state molecules, and the fast response time of TRISP makes it ideal for detonations. The technique has not been applied extensively and is difficult to implement, but our preliminary attempts have shown that we can do it with the proper laser apparatus. Broadband CARS is an alternative approach if the instrumental difficulties of TRISP cannot be overcome.

Laser induced fluorescence is, by now, a fairly well used technique for the quantitative probing of gaseous species. The advantage of using LIF is that it can detect very low concentration products whose presence in the detonation products is suspected but that cannot be reliably detected with mass spectroscopic methods. The sensitivity advantage can sometimes be offset by its specificity, so that only a limited amount of data can be accumulated during one trial.

To summarize, we have developed an apparatus of considerable versatility of measurement by which we can examine the products of detonation of small laboratory scale explosives. We have considerable evidence that the chemistry we are probing is characteristic of what is occurring in the reaction zone in some of the explosives, while for others the mass spectra we obtain is on a time scale as nearly characteristic of the detonation process as any other experimental measurements. The spectra that we report are considerably at variance with what model calculations predict, which suggests that the assumptions of equilibrium amongst the products is doubtful.

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Figure 1. Schematic arrangement showing essential features of the apparatus for the mass spectrometric examination of the reaction products from detonation. The figure is not to scale, and the text has a more complete description of the design considerations. Also reference 15 and others therein contain more detail .

Figure 2. An example of data obtained with the quadrupole mass filter. The vertical axis is the number of ions counted while the multichannel scaler was in a particular channel. For convenience the horizontal axis has been converted from channel number to the elapsed time from detonator excitation to the time that a particular channel number was being filled. Two sets of data are shown, one with the mass spectrometer set at $M=15$ and the other at $M=44$. The latter was scaled by a factor of 0.4

Figure 3. Time of flight spectra for two explosives averaged over all of the masses contained in the mass spectrum. RDX and TNT are being compared. The respective detonation velocities are shown with arrows, with that for RDX on the left.

Figure 4. A log-log plot of some of the important reaction product external variables calculated using a modeling program to represent the free expansion of those products from a pellet 3mm diameter and 3 mm high. The products have been given an equation of state somewhat characteristic of PETN. The particular mathematical cell considered here is at the cylinder end opposite to the detonation point. In the legend d stands for density, p for pressure, T for gas temperature, MFP for the mean free path for collisions in the gas, TBIM is the inverse of the rate for bimolecular exchange reactions, TUNI is the inverse of the rate for unimolecular decomposition. For the TBIM curve an activation energy of 10 kcal/mole and an A factor of 10^{12} was used. The short section of line that intersects TBIM and TUNI indicates the time at which quenching occurs.

Figure 5. A schematic of the optical telescope arrangement for taking Schlieren and shadowgraph photographs transverse to the motion of the freely expanding products of a detonating pellet. The beam diameter at the pellet is about 35 mm. The Schlieren aperture is slightly less than 1/3 mm (0.015 inches). The angles are exaggerated in the figure, the maximum angle of reflection from the curved mirrors being about 4-5 degrees.

Figure 6. Contains four slides of pairs of photographs consisting of a Schlieren photograph and a shadowgraph. The top single photo is of the field of view without a detonating pellet. The first pair is taken 2 microseconds after initiation, the second pair at 3, the third pair at 4 and the fourth pair at 5. The pellet was RDX. The small protrusions on the periphery of the circular window are caused by retaining rings that hold the windows in place.

Figure 7. Schlieren photographs of TATB, but these were taken with a fast framing camera. The sequence of each frame is from the bottom frame to the top frame, which is then repeated after being shifted from left to right. Each frame is one microsecond apart, and was exposed for 0.2 microseconds. A cw laser was used for illumination, at 514.5 nm and 1/2 watt.

Figure 8. The same as Fig. 7 except that the pellet was detonated with the ambient pressure at one atmosphere instead of at high vacuum.

Figure 9. A composite of the mass spectra obtained for the six explosive substances indicated. The vertical scale is relative to the most intense peak in each of the spectra, and are not scaled with respect to the other materials on the plot.

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Figure 10. This plot compares the experimental mass spectra for PETN and RDX with a set synthesized from equilibrium data.² Ion fragments expected for the given parent molecules are included in the synthesized plots, and we have omitted very small values for ease of plotting.

Figure 11. Same as Fig. 10, but for the explosives HNS and TNT.

Figure 12. The relative intensities of carbon clusters of size n , that is C_n , observed in products from HNS. Two different sets of conditions were used to obtain the data. The closed circles are for room temperature, unconfined expansion of the products after detonation. The open circles were obtained at 30 K with an overlayer of Xe covering the pellet to tamp the expansion. The dashed line represents an equilibrium distribution of carbon clusters at 3400 K and 0.01 atmospheres partial pressure of carbon vapor.

Figure 13. Sample data obtained by shocking solid nitric oxide with a PETN booster. These are all of the ions that were observed with any significant intensity. About 65% of the NO was consumed in the detonation, about 19% through the production of N_2 and O_2 .

Fig. 1

FIG. 2

FIG. 3

FIG. 4.

Optical Apparatus
Telescope Reflection Angles Exaggerated: 4-5° Max.

Fig. 5

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FIG. 1

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SUM TO 400 μ s

PETN EXPERIMENTAL

RDX EXPERIMENTAL

PETN SYNTHESIZED

RDX SYNTHESIZED

Fig. 11

CHM-VG-11,217

Fig 12

Fig. 13