Chemical Reactions in Strong Shock Waves[1]

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Strong shock waves, generated in shock tubes, provide a promising way of studying high temperature chemical reactions in gases. The heating by the shock wave is uniform, extremely rapid and intense so that the temperature may rise many thousands of degrees in a fraction of a microsecond. Observations of the effects of this heating on compounds like CH_3I and BrCN have shown extensive decomposition into such radicals as CH, C_2 and CN.

Introduction

When a strong shock wave passes through a gas, there is a large and almost discontinuous rise in pressure and temperature. Each gas molecule, in fact, has time for only about twenty collisions in changing from its initial state to the heated and compressed state, and in this short time the temperature may rise by several thousands of degrees. This rapid and homogeneous heating, which is otherwise difficult to obtain, provides a useful method of initiating and studying fast, high temperature reactions. This paper describes the methods we have used to bring about and study the decomposition of such simple substances as BrCN, CF_3I and CH_3I in strong shock waves.

Generation of Shock Waves.—Shock waves may be produced in a variety of ways—by the detonation of solid or gaseous explosives, by powerful sparks, or in a shock tube. We have investigated only the shock tube method because of its simplicity and adaptability and especially because of the uniform heating it provides. The shock strength can be varied easily over a wide range and there is no problem of contamination from the hot products of a detonation. Figure 1a shows a schematic representation of the tube. The compression chamber contains gas at a relatively high pressure and is separated from the expansion chamber by a thin diaphragm. When the d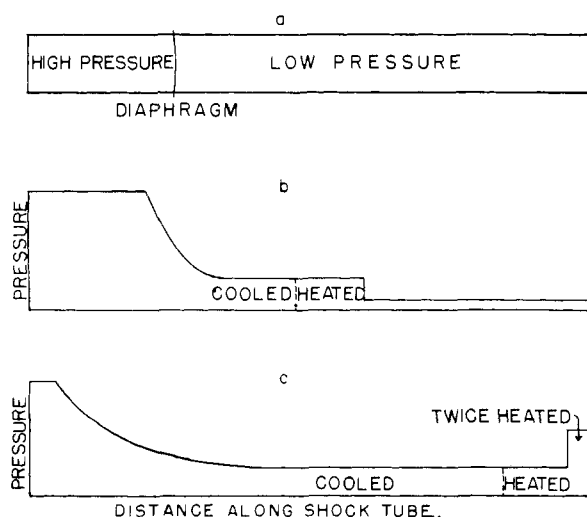iaphragm is punctured by a needle, a shock wave is formed as the gas from the high pressure section compresses the gas in the low pressure section. The shock wave moves with nearly uniform, supersonic velocity to the end of the tube where it is reflected and produces another region of still higher pressure and temperature. At the same time a rarefaction wave moves back from the diaphragm into the high pressure section. Figures 1b and 1c show the pressure distribution at two different times after the rupture of the diaphragm. Thus the gas originally in the high pressure section is cooled as it expands while the gas originally in the low pressure chamber is heated by compression twice—first in the original shock wave and then in the wave reflected from the end plate. A conventional time *versus* distance diagram (Fig. 2) provides a compact representation of what happens in a shock tube after the rupture of the diaphragm. The two regions of special interest are those of approximately uniform (uniform in the ideal case) heating behind the incident and reflected shock waves. Resler, Lin and Kantrowitz[2] have given an excellent description of the production of high temperature gases in shock tubes; while Bleakney, Weimer and Fletcher[3] and Geiger and Mautz[4] have described the construction of shock tubes. Carrington and Davidson[5] have been able
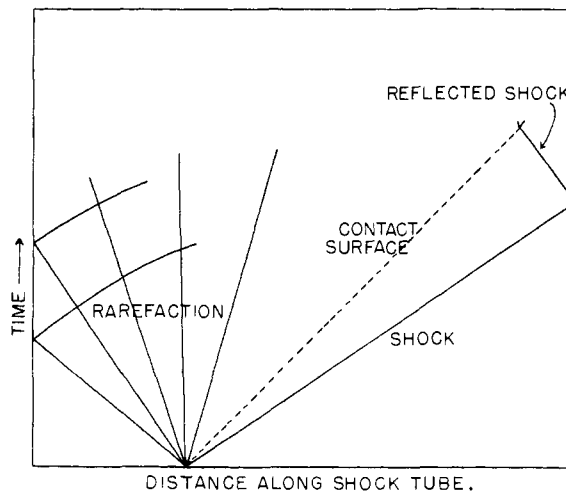

Fig. 1.—a, schematic of shock tube; b and c, pressure distributions in shock tube at two different times after rupture of the diaphragm.

Fig. 2.—Idealized flow in shock tube after rupture of the diaphragm.

(1) Assisted by the Office of Naval Research.

(2) E. L. Resler, S. C. Lin and A. Kantrowitz, *J. Applied Phys.*, **23**, 1390 (1952).

(3) W. Bleakney, D. K. Weimer and C. H. Fletcher, *Rev. Sci. Instruments*, **20**, 807 (1949).

(4) F. W. Geiger and C. W. Mautz, "The Shock Tube as an Instrument for the Investigation of Transonic and Supersonic Flow Patterns," University of Michigan, Engineering Research Institute Report, 1949, ONR Contract N6-ONR-232 T.O. IV.

(5) T. Carrington and N. Davidson, *J. Phys. Chem.*, **57**, 418 (1953).

to measure the very rapid rate of decomposition of N_2O_4 by making use of the extremely fast heating possible in a shock wave.

We have used two shock tubes of 1 inch and 2 inch internal diameter, respectively, which have high pressure chambers made from brass tubing ($\frac{1}{16}$ in. wall, 17 in. and 23 in. long) and low pressure sections of commercial glass pipe (Corning, 5 ft. and 8 ft. long) which have a rated maximum working pressure of 50 p.s.i. We have used diaphragms of cellophane (0.001 in.) or Kodatrace (0.0045 in.) single thicknesses of which can withstand pressures of 1.5 and 9 atmospheres, respectively, in our 1 inch i.d. tube. Four thicknesses of Kodatrace permit a pressure differential of 12 atmospheres in our 2-inch tube. The cellophane shatters more completely than the Kodatrace but according to Hollyer[6] this makes little difference in the properties of the shock when it has formed. A soft rubber gasket has been used between the brass tube and the diaphragm. We have limited ourselves to either hydrogen or helium in the compression chamber because hydrogen produces the strongest possible shock waves for a given ratio of pressures across the diaphragm while helium gives the next strongest shocks and has the advantage of being chemically inert. The essential property desired for the gas in the compression chamber is a high sound velocity (see ref. 2). Normally the pressure of hydrogen or helium has been from 1–12 atm. while the pressure of the gas to be heated has been from 0.1 to 100 mm. For our 2-inch tube this corresponds to from 3×10^{-5} to 3×10^{-2} mole of gas. Usually the pressure ratios across the diaphragm have varied between 10^2 and 10^5.

For a typical shock wave in the 1-inch tube: hydrogen is at a pressure of 1.3 atm., BrCN is at 0.6 mm. in the low pressure section, the velocity of the shock is 1.72 mm./microsec. (Mach 10) the time for the initial temperature rise is approximately 0.05 microsec. and the duration of uniform heating (before the reflected wave) is up to 1 millisec. depending on the original location of the gas in the glass tube. Our high pressure sections are long enough so that usually the rarefaction does not catch the shock before the reflected shock wave passes through all the gas which was originally in the low pressure section. Ultimately, however, the rarefaction reaches the heated gas of the low pressure section and begins to cool it. For cooling to occur sooner, it is only necessary to shorten the high pressure section so that the head of the rarefaction arrives earlier. In some cases cooling may be desired to begin even before the shock reflects from the end plate. The duration of the heating can be controlled easily by a piston in the high pressure section to vary its effective length. The difficulty with extremely long tubes is that there is a small but definite attenuation of the shock wave because of interaction with the tube walls.

The temperature of the hot gases is an especially important property to know. Resler, Lin and Kantrowitz[2] have shown that the available enthalpy per unit mass of the hot gas is approximately one-half the square of the shock velocity. That is: nearly all the kinetic energy of the undisturbed gas (considered with respect to the shock wave as a frame of reference) is converted to internal energy after passage through the shock wave. This means that from measurements of the shock velocity we can know the temperature if we can find the right heat capacity to use. Right at the shock front the correct heat capacity is just that which allows only for the rapidly excited translational and rotational degrees of freedom so that the "temperature" reaches a maximum and then falls as energy is distributed more slowly to the vibrational degrees of freedom. Finally when chemical reaction begins, our knowledge of the temperature becomes much less precise because of the unknown amount of reaction which is occurring. An endothermic reaction brings the temperature down, while if an exothermic reaction starts, the temperature can rise rapidly. For the shock wave in BrCN mentioned above the available enthalpy is approximately 36 and 41 kcal./mole for the incident and reflected shocks, respectively. At first when only translational and rotational energy is equilibrated the temperature would be approximately 7000 and 15,000°K. These values would then fall to approximately 2700 and 5100°K. when the vibrational degrees of freedom became equilibrated. Clearly considerable decomposition must then occur.

For hydrogen in the high pressure section (P_4) and several different gases varying in complexity from argon to normal octane in the low pressure section (P_1) Fig. 3 shows the calculated pressure ratios, P_4/P_1, required to produce incident shocks of given Mach numbers, and the enthalpy available for these Mach numbers from the incident and reflected shock waves. The shock Mach number is the ratio of the shock speed to the speed of sound in the undisturbed gas ahead of the shock. It is a convenient measure of shock strength because the velocity is the property of the shock most easily determined. In general, a low sound velocity for the gas to be heated means that a smaller P_4/P_1 will be required to produce the same Mach number; while for a given Mach number the enthalpy available decreases only relatively slightly in going from argon to more complex gases. Thus at a given Mach number the temperatures attained are approximately inversely proportional to the heat capacity of the gas—at Mach 10, if we assume no ionization occurs, argon is heated to 9500°K. while C_8H_{18} only to approximately 760°K. These calculations of P_4/P_1 and ΔH are based on the assumptions of ideal gas behavior, constant heat capacity, instantaneous thermal equilibrium, no interaction with the walls, and no work done by the gas on the diaphragm as it ruptures. The heat capacity used is that for vibration fully excited to the classical value but the changes would be very slight if equilibrium values were used instead. The deviation of experimental P_4/P_1's from those calculated is shown in Fig. 4 for shocks in CH_3I and N_2 (see refs. 2 and 6 for similar experiments in A and N_2).

Detection of Reaction in Shock Waves.—Several methods which can be used to study the regions of hot gas produced in the shock tube are: emission and absorption spectroscopy, measurement of relative velocities and densities and analysis of the final products of the reaction. A combination of these methods can yield a considerable amount of information about the substances formed during the decomposition. Here the situation is similar in many ways to that in flash photolysis which is being widely investigated, for instance by Norrish[7] and by Ramsay.[8] Both methods can produce large amounts of reaction in short times by the addition of large amounts of energy. However, for photolysis there must, of course, be absorption of light so if the substance itself is transparent an absorbing impurity must be added. This impurity may well

(6) R. N. Hollyer, Jr., "A Study of Attenuation in the Shock Tube," University of Michigan, Engineering Research Institute Report, 1953, ONR Contract N6-ONR-232 T.O. IV.

(7) R. G. W. Norrish, Z. Elektrochem., 56, 705 (1952).

(8) D. A. Ramsay, J. Phys. Chem., 57, 415 (1953).

affect the course of subsequent reactions. An advantage of photolysis is that the temperature can be kept almost constant by using a large excess of inert gas. With both methods one of the most interesting problems is the study of free radicals which are formed by the initial decomposition of simple parent molecules.
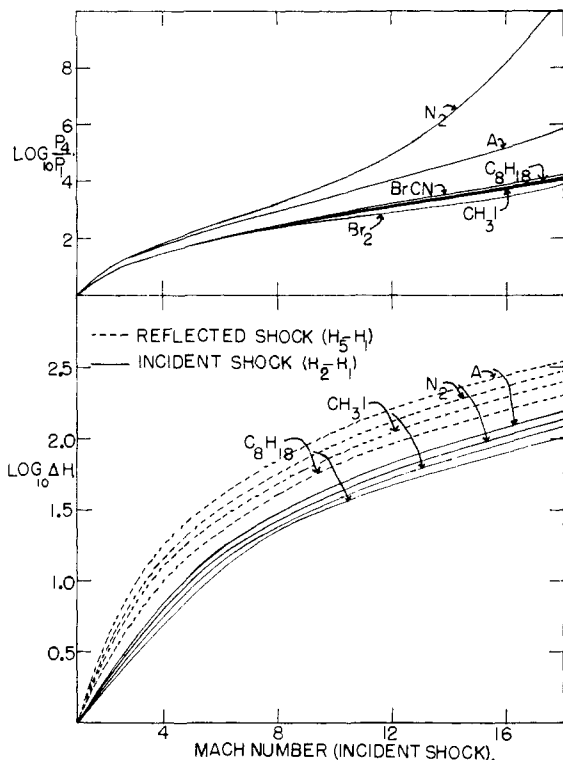

Fig. 3.—Bursting pressure ratios and enthalpy (kcal./mole) available in shocks of varying Mach numbers.

The most direct way of detecting and identifying substances which have known spectral bands is to examine the light either emitted or absorbed during the short time that the reactions are taking place. Many of the shock waves we have investigated are intensely luminous so that even with the very short exposures (approximately 20 microsec.) it is possible to record spectra on fast plates (Eastman I-D-(2) and I-N) using a large aperture spectrograph (Hilger f/1.5 Raman spectrograph E 612). Although it is possible, with the brightest shocks, to get spectra from the incident shock, usually the only satisfactory way is to use the much brighter region behind the reflected wave. Because of the small amount of light available the problem is much like that of Raman spectroscopy and can be helped by such devices as multiple pass sources.[9] Most of our spectra have been obtained by opening the camera shutter in a darkened room, and then setting off the shock, so that the emission is integrated over the whole shock. However, we have also used the spectrograph as a monochromator and followed the light emitted from a given region of the spectrum as a function of time with a photomultiplier. (Compare Norrish, Porter and

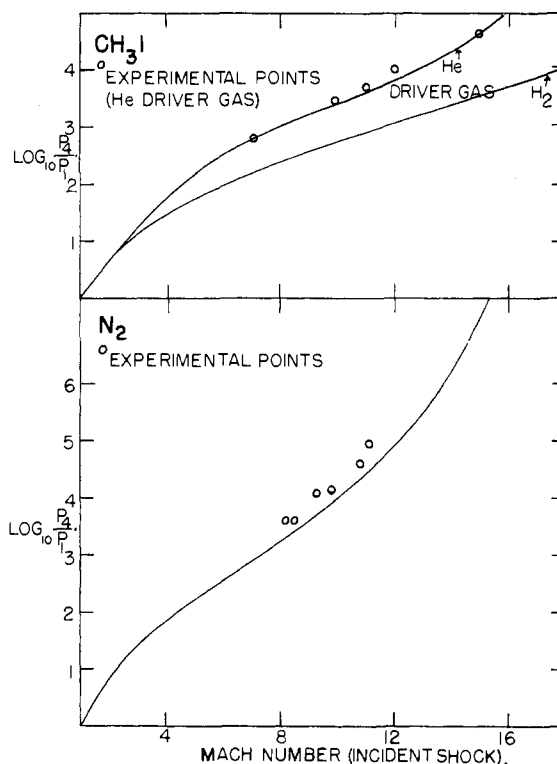Thrush,[10] in their study of flash initiated combustions.)

Fig. 4.—Calculated and experimental bursting pressure ratios for shocks of varying Mach numbers.

Absorption spectra should provide information to supplement that from emission spectra in several ways. First, if the molecules which emit are in thermal equilibrium with the ground state, the concentration of absorbing molecules should be higher by a factor of approximately $e^{h\nu/kT}$ (where ν is the frequency of the light emitted) which can be a very large number. However, if the radicals are formed in excited states and emit before they are de-excited by collision, there is no such favoring of absorption. Thus a comparison of relative intensities may provide an indication of the original state in which the radical is formed when the parent molecule decomposes. Second, an advantage of absorption spectra is that time resolution can be achieved by varying the time after passage of the shock at which the short duration light source is turned on. Similar time resolution with emission is more complicated to obtain, for it is necessary either to have a fast shutter or to get motion of the image relative to the film as in a drum camera. Of course, the change of absorption with time for a given region of the spectrum may also be observed by using a steady light source, a monochromator or filter, and a phototube.

Some of the measurable properties of the shock wave, for instance the density behind the reflected wave and the velocity of the reflected wave, are quite sensitive to the presence of dissociation or ionization in the gas. (See ref. 2 for the calculated

(9) H. L. Welsh, C. Cumming and E. J. Stansbury, *J. Optical Soc. Am.*, **41**, 712 (1951).

(10) R. G. W. Norrish, G. Porter and B. A. Thrush, *Proc. Roy. Soc. (London)*, **A216**, 165 (1953).

effects for the ionization of argon.) When a shock is luminous the reflected velocity can be measured (*e.g.*, with a drum camera) and the dissociation energy estimated by comparison with the reflected velocity calculated for various dissociation energies. A complicating but very interesting factor here is the question of the extent to which thermal equilibrium is reached. Also for luminous shocks it is possible to estimate roughly the ratio of the original density in the low pressure section to the density behind the reflected shock by taking a drum camera picture of the end of the tube and noting the length of the bright region of the reflected shock compared to the length of the low pressure section. Here turbulence is assumed negligible and the end of the bright region is taken to be the position of the contact surface (which separates the hydrogen from the heated gas) when the reflected wave reaches it. Pictures of strong shock waves in several substances show that the brightness is often fairly uniform over a region at the end of the tube. More work will be required to explore the usefulness of these methods.

Important though less direct information is available from analysis of the final products of the reaction after the shock is over. Here, as in flash photolysis, the products may be quite different from those formed in ordinary decompositions because of the rapid heating and the high concentrations of intermediates which are formed.
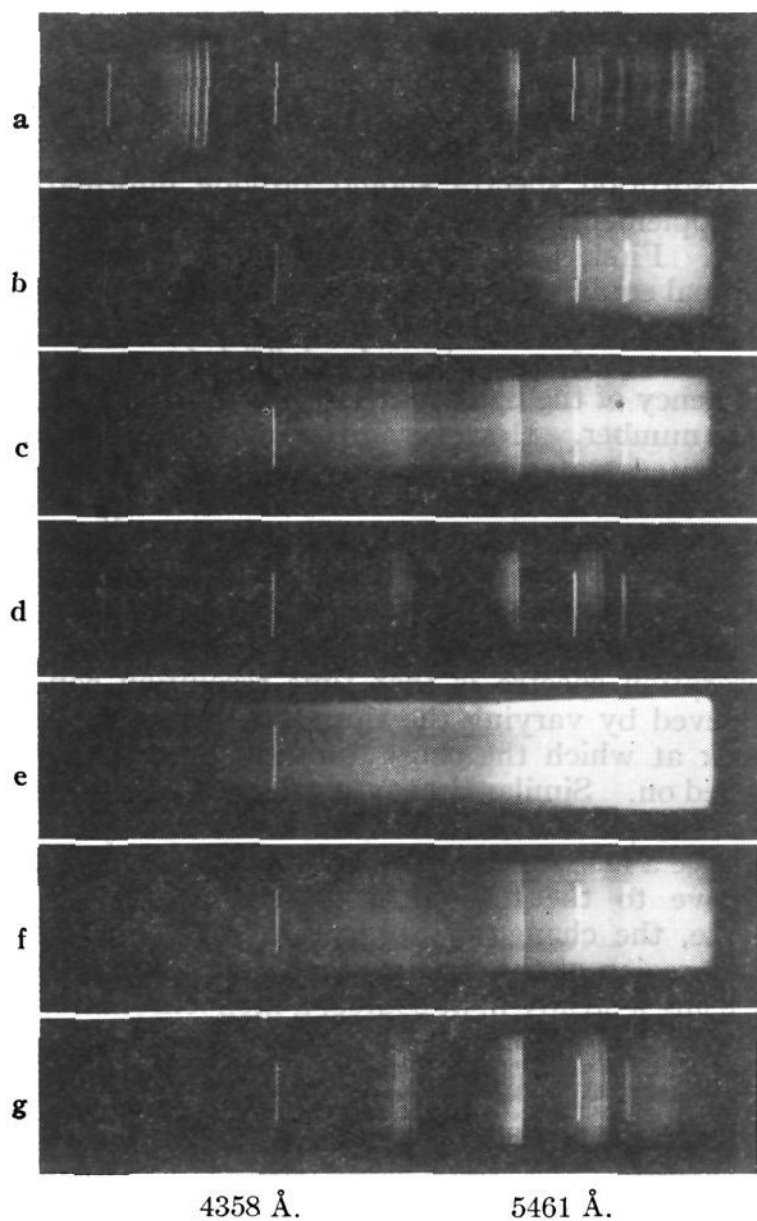

4358 Å.   5461 Å.

Fig. 5.—Emission spectra from shocks in: a, BrCN; bcd, CH$_3$Br; efg, CF$_3$Br.

Application of Methods of Studying Reactions behind Shock Waves.

—We have examined the frequencies of the light emitted by a variety of simple substances decomposed in strong shock waves. With BrCN where the C–Br bond energy is about 80 kcal./mole or ClCN (C–Cl approximately 94 kcal./mole) both the red and violet systems of CN and the C$_2$ Swan bands show up strongly. The relative intensity of the violet to the red bands decreases noticeably as the shock strength decreases. Figure 5a shows a typical spectrum taken of the region behind the reflected wave of a shock in BrCN with hydrogen as the driver gas and with P_4/P_1 equal to 1000. The shorter reference lines are from a mercury arc lamp. By using a photomultiplier and a monochromator we have found that in a similar shock the light emitted from CN comes appreciably earlier than that from C$_2$. Figure 6 shows light intensity in arbitrary units plotted against time for the CN bands near 4216 Å. and the C$_2$ bands near 4737 Å. Although the temperature is not constant and these intensities therefore have no direct relation to concentrations, nevertheless, it is tempting to suppose that $2CN \rightarrow N_2 + C_2$ which would be an interesting reaction to study. H. B. Palmer in this Laboratory has shown that absorption spectra also can be obtained from shock waves. By synchronizing a short duration exploding wire source with a shock in BrCN he has found absorption due to CN. After certain of these runs there is on the tube walls a black deposit which we believe to be carbon and sometimes a white deposit which may be a polymer of CN.
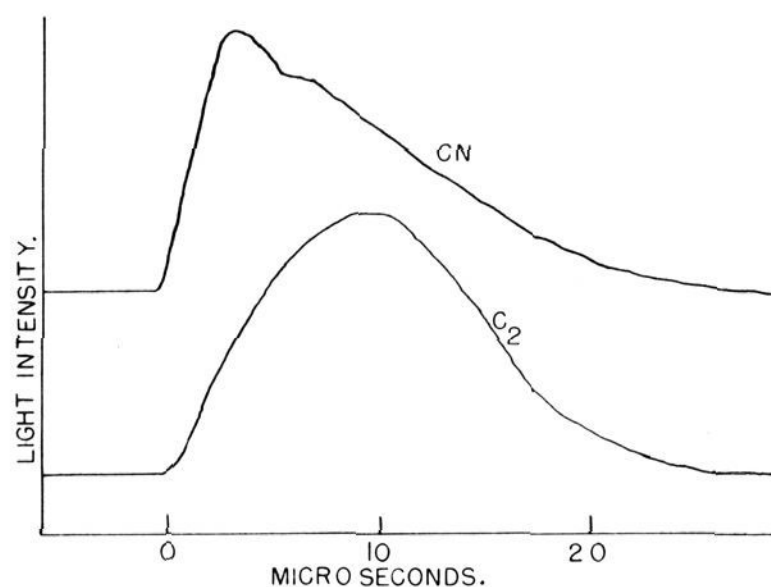

Fig. 6.—Variation with time of light emitted by CN and C$_2$ formed by decomposition of BrCN.

In an effort to observe the spectra of CH$_3$ and CF$_3$, we have tried similar shocks in CF$_3$Br and CH$_3$Br, which also give intense emission (somewhat less intense, however, than that from BrCN). Here there is an interesting change in the character of the spectrum as the shock strength increases. For a pressure ratio across the diaphragm of 2000 (hydrogen as driver gas) the only noticeable emission is a continuum intense in the red and falling off in the green. Increasing the pressure ratio twice by factors of two (P_4 constant, P_1 decreasing) brings out the C$_2$ Swan bands and in the case of CH$_3$Br the CH system at 4300 Å. while the continuum becomes

relatively much less intense. Figure 5bcd and efg show this change for CH_3Br and CF_3Br, respectively. The spectra from CH_3I and CF_3I are like those for the bromides except that they are noticeably more intense. That from CH_2Br_2 is very much like that from CH_3I. More work will be necessary to resolve the time sequence of emission from the CH, C_2 and the continuum, but it is intriguing to think that the continuum may be due to CH_3.

After these runs the odor of halogen is distinctly noticeable in the shock tube and with the iodides there is a considerable deposit of solid iodine as well as carbon on the tube walls. Chemical analysis by titration with thiosulfate showed that from one half to two thirds of the I in the original CH_3I was recovered as molecular I_2 for shocks with a range of pressure ratios (with helium as the driver gas) of 150–5000 (Mach 5–15). This shows that the extent of decomposition is considerable. After one run (Mach 7) the products were condensed at liquid nitrogen temperatures to separate them from the helium of the compression chamber; an infrared spectrum of the vapor showed absorption at 730 and 949 cm.$^{-1}$ characteristic of bands of acetylene and ethylene. The sample is acid and the spectrum also shows the 2310 cm.$^{-1}$ band of HI. Much more precise work will be required to get good estimates of the relative amounts of these and other substances which may be present.

Conclusion

The use of a shock tube for work in high temperature chemistry has certain limitations—it is effectively restricted to small amounts of gases which can be heated for only short times—but on the other hand there are unusual advantages. An enormous range of temperatures (up to many thousands of degrees) is easily available without the usual problems of insulation, the apparatus is simple to construct, the heating is extremely rapid, the ultimate cooling slower but still rapid, and perhaps most important the heating is homogeneous. Thus the behavior of molecules can be studied at temperatures comparable to those in detonations but without the complications arising from the presence of other substances.

Appendix

The following is a list compiled from various sources[2-4] of formulas, applicable to shock tube work, which are derived on the assumption of the ideal gas equation of state, constant heat capacities, instantaneous removal of the diaphragm, and no interaction of the gases with the walls of the tube.

(1) Bursting pressure required for a given shock pressure ratio

$$\frac{P_4}{P_1} = \frac{P_2}{P_1}\left[1 - \frac{a_1}{a_4}\cdot\frac{\gamma_4 - 1}{\gamma_1 - 1}\cdot\frac{\frac{P_2}{P_1} - 1}{\sqrt{\left(\frac{2\gamma_1}{\gamma_1 - 1}\right)\frac{P_2}{P_1}\left(\frac{\gamma_1 + 1}{\gamma_1 - 1} + \frac{P_1}{P_2}\right)}}\right]^{-2\gamma_4/(\gamma_4 - 1)}$$

(2) Mach number for a given shock pressure ratio

$$M_1 = \frac{U_1}{a_1} = \sqrt{\frac{(\gamma_1 + 1)\frac{P_2}{P_1} + \gamma_1 - 1}{2\gamma_1}}$$

(3) Shock density ratio for a given shock pressure ratio

$$\frac{\rho_2}{\rho_1} = \left[\frac{P_2}{P_1}(\gamma_1 + 1) + \gamma_1 - 1\right]\Big/\left[\frac{P_2}{P_1}(\gamma_1 - 1) + \gamma_1 - 1\right]$$

(4) Reflected shock velocity in terms of the pressure ratio of the incident shock

$$U_R = a_1\left[2 + \left(\frac{2}{\gamma_1 - 1}\right)\frac{P_1}{P_2}\right]\Big/\sqrt{\left(\frac{2\gamma_1}{\gamma_1 - 1}\right)\frac{P_1}{P_2}\left(\frac{\gamma_1 + 1}{\gamma_1 - 1} + \frac{P_1}{P_2}\right)}$$

where following reference 2

a = speed of sound
γ = ratio of specific heats
M_1 = U_1/a_1 = shock Mach number
P = pressure
ρ = density
U_1 = propagating speed of the incident shock relative to the shock tube
U_R = propagating speed of the reflected shock relative to the shock tube

subscripts indicate the following regions in the shock tube

1, undisturbed gas ahead of the shock
2, heated gas behind the shock
4, undisturbed gas in the high pressure section
5, twice heated gas behind the reflected wave

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