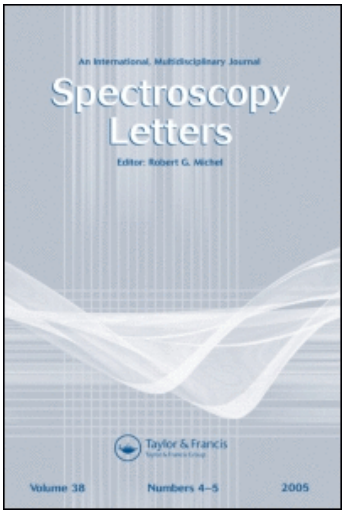


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# Spectroscopic Studies of Chemical Reactions in Strong Shock Waves

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# SPECTROSCOPIC STUDIES OF CHEMICAL REACTIONS IN STRONG SHOCK WAVES

Key Words: Shock Tube, Diaphragm, Shock Wave, Emission Spectroscopy, Band Spectra, Chemical Reaction

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## ABSTRACT

Shock tube provides a promising tool of studying high temperature chemical reaction in gases. The heating by shock wave is uniform, extremely fast and intense. So that the temperature may rise thousands of degrees in a fraction of a second. Observations of the effects of this heating on $C_6H_6$ has shown extensive decomposition into $C_2$ and CN.

## INTRODUCTION

In recent years there has been a growing interest in the production of high temperature in gases using a shock wave technique. This is of particular interest in the studies of properties of gases at high temperature and various associated

phenomena, such as, atomic and molecular exertation, ionization, dissociation, in addition to the aerodynamic problems. This paper describes the method we have used to bring about the decomposition of simple substance like $C_6H_6$ in strong shock waves. Greene[1] examined the emission spectra from shock exertation of aliphatic vapours of the following types:

$$XCN \text{ (where X = Br or Cl)} \quad (1)$$

$$CX_3Y \text{ (where X = H or F, Y = Br or I).} \quad (2)$$

He reported the presence of $C_2$-swan band at 4315 Å in case of (2). On the other hand, Fairbairn and Graydon[2] reported spectra from shock experiments covering a wide range of aliphatic compounds. They discovered that in these emission spectra, carbon particle continuum and $C_2$-swan bands were dominating. Sometimes however, OH and CN bands appeared, but no trace of CH band could be detected even for the molecules containing C and H.

The current investigation shows the decomposition mechanism of $C_6H_6$ into $C_2$ and CN kinetics behind the reflected shock waves. After the experiment abundant black deposits were found on the tube walls. CH system at 4358 Å however is not observed as reported by Johnson and Campbell[3].

Results obtained from shock tube work were compared with the results of Knight and Rink[4] and Tsang et al.[5] Comparison is also

zation temperature of benzene ($C_6H_6$), it seems more probable that the shock treatment causes the beginning of the pyrolysis of two of the four essential reactions:

$$C_6H_6 \longrightarrow C_6H_5 + H \tag{3}$$

$$C_6H_5 \longrightarrow C_2H_2 + C_4H_3. \tag{4}$$

At higher temperatures the reaction between $N_2$ (available as an impurity from commercial argon) and $C_2H_2$ may explain the appearance of CN violet band[15].

A strong possibility of the formation of $\overset{*}{C}_2$ emitters is from the dissociation of CN molecules in which $C_2$ molecules are formed as an intermediate product which subsequently dissociates to atoms at equilibrium. An alternative path to the formation of $C_2$ emitters may involve an exchange of hydrocarbon radical during which CH is formed as typified by the reaction:

$$\begin{aligned} CH + CH &\longrightarrow \overset{*}{C}_2 + H_2 \\ C_2 + N_2 &\longrightarrow C_2N_2 \\ C_2N_2 + Ar &\longrightarrow 2CN + Ar. \end{aligned} \tag{5}$$

The dissociation of CN in an Ar diluent was investigated by Slack[15] by shock heating $C_2N_2$($4400 < T°K < 13{,}000$). Dissociation rate co-efficients are the same as given in reaction (5).

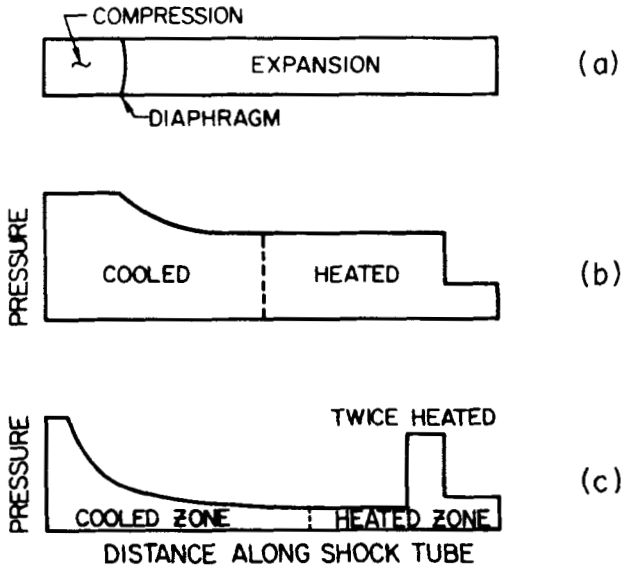


Figure 1. a) Schematic diagram of shock tube; b and c) Pressure distributions at two different times after bursting of the diaphragm.

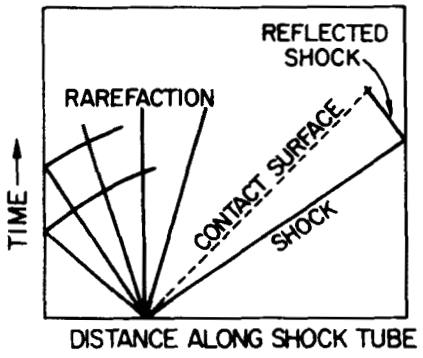


Figure 2. An idealized flow in shock tube after rupture of the diaphragm.

are those ahead and behind the shock front. Resler et al.[8] have given an excellent description of the production of high temperature gases in shock tube; while Bleakney et al.[9] and Curzon and Phillips[10] have described the construction of shock tubes. Slack et al.[11] have been able to measure the very rapid rate of decomposition of $C_2N_2$ by making use of the extremely fast heating possible in a shock wave.

We have constructed one shock tube of 2-inch internal diameter and 18 inches long, made from a galvanized iron low pressure section also made from the similar type of material of 54 inches long. We have used diaphragms of cellophane (.001 inches to .01 inches), single thickness of which can withstand pressure up to 5 atmospheres in two-inch tube. A soft "O" ring of diameter 3-inch has been used between the flanges and the diaphragm[12,13]. We have limited ourselves to hydrogen only in the compression chamber because hydrogen produces the 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[10]. Normally, the pressure of hydrogen has been from 1 - 5 atm. while the pressure of gas to be heated has been from .01 to 44 mm with a trace of argon. Usually the pressure ratios across the diaphragm have varied between $10^2$ and $10^3$.

The temperature of hot gas is an especially important property to know, which means that from the measurement of shock velocity we can know the temperature if we can find out 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 translation and rotational degrees of freedom so that the temperature reaches a maximum and then falls monotonically as the energy distributed to the vibrational degrees of freedom. For the shock waves in $C_6H_6$ mentioned earlier the available enthalpy is approximately between 35 - 45 Kcal/mode for the incident and reflected shocks respectively. At first translational and rotational energy is equilibrated when the temperature would be approximately 6000 and 16,000° K. These values would be approximately 2500 and 500°K when vibrational degrees of freedom become equilibrated and hence decomposition must then occur. For hydrogen in the high pressure section ($P_2$) and the vapour of $C_6H_6$ varying separately with argon in the low pressure section ($P_1$). The calculated pressure ratios ($P_2/P_1$) required to produce incident shock in is about 290 at Mach number 16. These calculations of ($P_2/P_1$) are based on the assumption of ideal gas behavior, constant heat capacity, instantaneous ruptures of the diaphragm and no interaction between the walls of the shock tube.

## STUDIES OF SPECTRUM

Hilger method quartz spectrograph was used to photograph the spectrum of incident radiation with a lit width of the order of .02 mm - .03 mm. The shutter of the spectrograph was kept open in a darkened room before setting off the shock, so that emission is integrated over the whole shock. Fig. 3 shows the CN and $C_2$ bands which arises due to the transistion of $B^2\Sigma^+ - X^2\Sigma^+$ and $A^3\Pi_g - X^3\Pi_u$. The energy transfer during the process was 3.2 ev. Band H state lies about 25751 $em^{-1}$ and 19306 $em^{-1}$ above the ground state[14].

## CHEMICAL REACTIONS BEHIND THE SHOCK WAVES

From the spectroscopic studies of $C_6H_6$ molecules we have obtained CN and $C_2$ bands. In view of the much lower volatili-

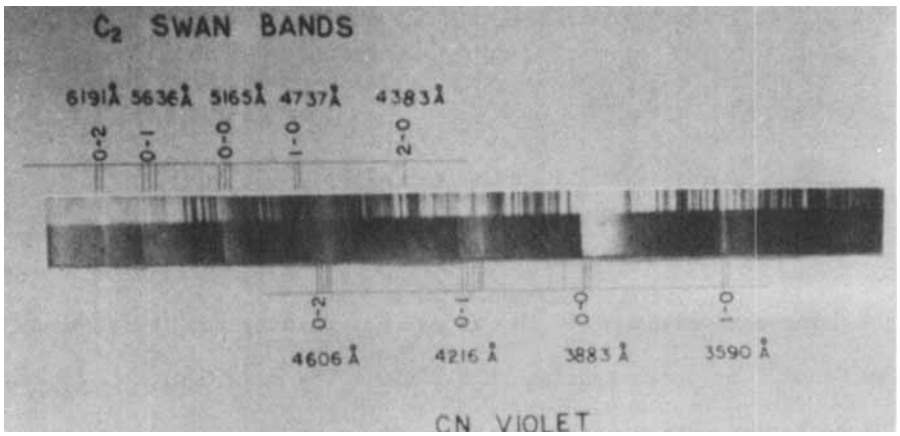


Figure 3.

## CONCLUSION

Results obtained through shock tube work were compared with results of Knight and Rink and also from Bauer and Watt's CN kinetics by reflected shock wave. But it is not clearly understood that after each run there is a black deposit which may be a polymer of CN. So this can be an attempt for the future course of study by using these compounds.



## ACKNOWLEDGEMENTS

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