SHOCK-INDUCED DECOMPOSITION OF CARBON DISULFIDE

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**Title**: Shock-Induced Decomposition of Carbon Disulfide

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**Abstract**

The purpose of this work is to study the shock-induced chemical decomposition of liquid CS$_2$. Studies of mechanical response have shown that the liquid under compression transforms to a higher density form. Past work has shown that this transformation occurs under static pressure at 45 kb and 175°C. Previous shock experiments have shown that a similar transformation occurs in a single shock at approximately 60 kb and 1000°C. Sheffield at WSU has shown that the transformation occurs in a reflected shock at pressures...
greater than 75 kb and at temperatures greater than 750°C. The transformation or reaction time was determined by Sheffield in various ways and found to decrease from about 400 nsec at 79 kb to less than 10 nsec at 130 kb. At the lower pressures there is an induction time decreasing from 300 nsec at 79 kb to less than 6 nsec at 106 kb.

In the year just completed attention has turned from mechanical to optical aspects of the reaction. A major effort has gone into repair, installation and calibration of the time-resolving spectrograph to be used for absorption spectroscopy. Similar effort has been expended on measurement of light emitted from the CS$_2$ when shocked. This work has produced new information on radiation from shocked PMMA, but it hasn't yet been determined whether or not the CS$_2$ emits characteristic radiation when shocked. Finally, a significant effort was devoted to study and evaluation of shock tube experiments on the kinetics of CS$_2$ decomposition. It's concluded that the results have little bearing on expectations for shocked liquid CS$_2$. 
SUMMARY

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I. PROBLEM STATEMENT

In a 1977 paper, Yakusheva, Yakushev and Dremin reviewed work on the transparency and shock compression of several carbon-bearing materials. They proposed that there is sufficient justification to suppose that loss of transparency under shock and existence of a cusp in the Hugoniot P-V curve are correlated. They noted that in such cases the carbon bonds are unsaturated and proposed that either transparency loss or a cusp in the Hugoniot is evidence of pressure-induced pyrolysis of unsaturated carbon compounds, leading to the formation of free carbon.

Sheffield, here at Washington State University, had undertaken a study of mechanical parameters of CS$_2$ under shock conditions, having postulated that a cusp in the Hugoniot at 60 kb reported by R. Dick corresponds to chemical decomposition of the compound. His work has set in motion a continuing effort to investigate as thoroughly as possible the physical, chemical and optical events associated with this shock-induced transition of liquid CS$_2$ to a higher density state.

Carbon disulphide is a colorless liquid at room temperature and atmospheric pressure. It has a density of 1.26 g/cc and heat of formation from graphite and solid sulfur of 22 kcal/mol, indicating that it is metastable under these conditions. P. W. Bridgman, in 1942, reported that, under hydrostatic pressures greater than 45 kb and temperature of 175°C or more, there is a "slow and irreversible change to a black solid, permanent under atmospheric conditions - a new form of CS$_2."$ The density of this new substance he reported to be 4% greater than an aliquot mixture of carbon and sulfur.

Later work by Whalley, Butcher, Alsop, Weston, and Gebbie, and Chan and Jouscher indicated that this new material is composed of two different substances, and that it decomposes to carbon and sulfur at 170°C and atmospheric pressure with an energy of release of 16 kcal/mol.
Afanasenkov and associates calculated a Hugoniot curve for a mixture of carbon and sulfur and found that it agreed with measurements by R. Dick at high pressures. They also measured the brightness temperature of CS$_2$ shocked to the high density state and found it to be approximately 500°C higher than their calculated values. From both these results they inferred the existence of a shock-induced decomposition with release of heat.

Sheffield, in a procedure inverse to that of Afanasenkov et al., inferred an equation of state for the decomposition products from R. Dick's Hugoniot data at high pressures. His best fit corresponds to a density at room temperature which is in close agreement with the density of a statically compressed mixture of carbon and sulfur. The equation of state of the products, combined with a similar equation of state of CS$_2$ shows the latter to be metastable or unstable throughout the entire range of pressures and temperatures accessible by shock.

The kinetics of CS$_2$ decomposition in the vapor phase has been studied using shock tube and optical spectroscopy techniques. The two principal works are by Gaydon and colleagues, who measured absorption spectra, and Arnold and colleagues, who measured emitted light. In the former work, absorption was measured for CS$_2$, CS and S$_2$. The latter two appeared as the formed disappeared, and the results were compatible with the assumption that reaction was occurring according to

$$\text{CS}_2 \rightarrow \text{CS} + \frac{1}{2} \text{S}_2 \quad (1)$$

Arnold et al. measured light emission throughout the visible spectrum. They felt their results to be incompatible with Eq. (1) and proposed

$$\text{CS}_2 + \text{CS}_2 \rightarrow \text{CS}_3 + \text{CS} \quad (2)$$

$$\text{CS}_3 + \text{M} \rightarrow \text{CS}_2 + \text{S} + \text{M} \quad (3)$$

They also found an induction time preceding the reaction for temperatures below
2600°K, whereas Gaydon et al. found no evidence of induction. Both groups of workers agreed that the reaction was second-order in CS₂ concentration, with reaction constants

\[ k_2 = 10^{14.2} e^{-43.7 \text{ kcal/RT}}, \quad \text{Gaydon et al.} \]

\[ k_2 = 10^{11.53} e^{-45.2 \text{ kcal/RT}}, \quad \text{Arnold et al.} \]

In experiments where CS₂ vapor has been excited by electron impact or UV light, it appears to be common to observe spectra of CS and S but not S₂. This is peculiar because the heat of formation of S₂ relative to S under standard conditions is about -34 kcal/mol.

The problems faced in the WSU program have been to, first, determine what parameters which will yield significant chemical information for liquid CS₂ can best be measured in a shock environment where pressures may exceed 100 kb for only one or two microseconds before the assembly is destroyed, and, second, to devise an experimental design which will allow the measurements to be made.

At the time this research was started, we had on loan from the U.S. Air Force a vacuum spectrograph coupled with a rotating mirror streak camera which is capable of providing a record of the evolution in time of the spectrum of any light source presented, limited in wavelength only by the quartz lens in the streak camera and the sensitivity of film. This instrument had not been operated since it had arrived on campus, nor for a number of years before that. It was evident that if it could be made to operate, it could provide exactly the kind of information we require to unravel the chemical kinetics. We therefore set about designing an experiment which would be compatible with the requirements for absorption spectroscopy, and which would also provide the "global parameters" of the experiment. That is, the regimes of pressure and temperature for which the rate of reaction was in a range suitable for study with time resolution in the range 20 to 50 nsec.
This initial phase of the research, carried out by S. A. Sheffield, was completed in the spring of 1978. The major results are described in the Annual Summary Report for this contract, 4/1/77 to 3/31/78. They are briefly summarized here.

Design of the experiment is illustrated in Fig. 1. A high impedance impactor moving at high speed is allowed to strike the plane face of a PMMA cell filled with CS$_2$. The shock induced in the PMMA is shown as state "0" in Fig. 1c. This shock passes through the PMMA and transmits the shock state labeled "1" into the CS$_2$. The CS$_2$ shock travels through the cell at a pressure below that required to produce decomposition and reflects from the sapphire back plate of the cell on reflection; the shock state "3'" is produced in the unreacted CS$_2$, and this decays to state "3" as reaction proceeds. As the reflected shock travels back through the cell, it breaks into two waves: a precursor in CS$_2$ corresponding to some state "2" and the reaction shock carrying the material to state "3" in the reaction products.

By introducing EM velocity gages at various positions in the cell, Sheffield was able to

1) detect the decay from 3' to 3;
2) trace the development of the three-wave structure;
3) record the risetime of the reaction shock in the reflected wave.

In addition to this, he recorded an unexpected, quasi-coherent electrical noise which appears to be associated with the reaction and decays approximately as the reaction decays.

In items 1, 2, and 3 above all give information about reaction rate. Characteristic reaction times vary from less than 10 nsec when state 3' is greater than 100 kb to several hundred nanoseconds for 3' = 80 kb. Temperatures in the unreacted CS$_2$ range from about 1000 to 1200°K. At the lower pressures there is clear indication of an induction time preceding the reaction. It ranges in magnitude up to 300 nsec.

At the completion of this phase of the work Dr. Sheffield went to the Sandia
Fig. 1  Experimental Sketch and Shock Diagrams for the CS$_2$ Experiments. (a) shows the experimental layout, i.e. a sapphire impactor hitting a CS$_2$ cell with a PMMA front and a sapphire back. (b) shows the direction of the shocks produced and the various states achieved.
Fig. 1 (continued). (c) shows the states achieved in pressure-particle velocity space. Notice the relaxation that takes place from state 3' to state 3 as the reaction proceeds.
Laboratories in Albuquerque, and our attention at WSU turned to the problems of spectroscopy.

II. THE TIME-RESOLVING SPECTROGRAPH

This instrument was manufactured by Beckman and Whitley in San Carlos, CA (since absorbed by the Cordin Co.). It consists of the Model 339B Continuous Writing Streak Camera coupled with a Model 1500 Spectrographic Dispersion Unit. Except for a single quartz lens in the camera, all optical components are reflectors. It can be evacuated, and with the proper grating it can operate from deep in the ultraviolet well into the infrared.

Physically the instrument is a monster, being about 6 ft by 4-1/2 ft by 3 ft overall, weighing about 1500 lbs. It was necessary to have the turbine for the camera mirror rebuilt, and this was done by the Cordin Co. The original grating was ruled at 150 lines/mm, which is suitable for the visible and infrared, and this has been replaced by a 600 lines/mm grating with peak efficiency at about 3000 Å. Internal reflectors had become coated with oil, and it was necessary to disassemble the instrument and clean all reflecting surfaces.

The instrument has been installed on a platform above the gun in which the projectile is accelerated. It is situated so that it looks vertically downward into the target chamber. In operation, light from a flash lamp will be allowed to pass through the sapphire back plate of the CS₂ cell, through a thin layer of CS₂ bounded by the sapphire and a reflecting foil in a plane parallel to the back face of the sapphire. After reflecting from the foil it will again traverse the thin layer of CS₂ in which absorption is occurring and be conveyed to entrance slit of the spectrograph. The primary limit on time resolution is provided by thickness of the layer between sapphire and reflector. For a layer 0.1 mm thick and a reflected shock velocity of 4 mm/µsec, the time required for the shock to traverse the layer is
.025 μsec, and the absorption measurement will be averaged over this time interval. This is probably about the best that can be achieved. Whether or not it is possible to do this well remains to be determined.

The limiting time resolution of the camera is 5 nsec. The time resolution which can be realized depends on spectral resolution, light intensity, and film sensitivity. Limiting spectral resolution with the 600 lines/mm grating is about 2 Å. In our initial experiments, no such resolution is required. With a blackbody light source at 6000°K and spectral resolution of 64 Å, an exposure of 28 nsec puts .05 ergs/cm² on the film, which is enough to insure adequate exposure with no extraordinary measures taken to sensitize the film. Our presently available source is a Xe flash lamp which corresponds approximately to a blackbody at 6000 degrees. It is adequate for preliminary purposes, but if reflection and absorption losses in the cell are severe, it may be submarginal. In that case, or if greater spectral resolution is required, it will be necessary to provide a higher temperature source. Some work has been done toward this end.

Calibration of the camera-spectrograph has turned out to be a major task. It is approaching an end, and we expect to begin preliminary absorption experiments soon.

III. SHOCK-STIMULATED RADIATION

There have been some reports of light emitted from shocked solids and liquids. It has been largely from experiments in which shock pressure was several hundred or more kilobars. In most cases it has been identified as blackbody radiation. In a few experiments non-equilibrium radiation has been reported.

Five experiments have been performed looking for light emission associated with the onset of reaction when the initial shock reflects from the sapphire back plate. The results are interesting because unexpected. They haven't yet provided much information about CS₂. They are listed in the following table.
**Light Emission Experiments**

<table>
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<th>No.</th>
<th>Cell</th>
<th>Spectral Region</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard, CS$_2$ filled</td>
<td>visible</td>
<td>light</td>
</tr>
<tr>
<td>2</td>
<td>Standard, CS$_2$ filled</td>
<td>blue and red</td>
<td>light</td>
</tr>
<tr>
<td>3</td>
<td>CS$_2$ replaced by PMMA</td>
<td>blue and red</td>
<td>light</td>
</tr>
<tr>
<td>4</td>
<td>Solid cell of black PMMA</td>
<td>blue and red</td>
<td>light</td>
</tr>
<tr>
<td>5</td>
<td>Brass cell filled with CS$_2$</td>
<td>blue and red</td>
<td>no blue</td>
</tr>
</tbody>
</table>

The experiments involved photomultiplier tubes set up to look through the sapphire back plate along the cell axis. In the first experiment a single PM tube was used; in the others there were two tubes: one with a blue low-pass filter and one with a red high-pass filter. Optics were glass so the total spectral range was little more than the visible.

In all experiments but the last there was a great deal of light. In each case the record of PM output vs time could be closely correlated with shock events in the cell. In the first experiment there was an intense flash at the instant of impact, presumed due to compression of residual gas between impactor and target. This was followed by a period of decaying intensity and a second, weaker flash when the first shock reflected from the sapphire back face. Following this, the intensity increased with time as if optical depth were large and the increase in shocked volume produced a corresponding increase in observed light. Then this, too, was quenched at about the time the rarefaction from the back of the sapphire impactor reached the reflected shock. This event was followed by a long, intense light which might reasonably have been associated with the breakup of the cell. The close time correlation of the various events with intensity was encouraging and we elected to do a second CS$_2$ experiment.

In the second CS$_2$ experiment blue and red filters were added to separate thermal radiation (which peaks in the infrared) and any characteristic radiation in the blue
or near ultraviolet. The impact surface was shielded to eliminate radiation from compressed gases. In this experiment, too, there was a great deal of light, but red and blue outputs were uncorrelated, and neither correlated properly with shock events. Something had gone wrong with the timing. It was evident, however, that there were a lot of light sources other than the shocked CS$_2$, so we decided to do a control experiment with PMMA replacing the CS$_2$. In this third experiment there was also a lot of light in both blue and red. Records from the two PM tubes were well-correlated and were time-correlated with shock events. Light increased sharply when the first shock reflected from sapphire, and thereafter followed a course similar to that of the first CS$_2$ cell, but with greater intensity. PMMA is obviously unsuitable cell material for a light emission experiment.

Experiment no. 4 was a second control experiment with the cell made entirely of black PMMA. It produced even more light than the clear PMMA.

The cell in experiment no. 5 was constructed of brass and the optics were arranged so the PM tubes looked through a window in the side of the cell. This arrangement has the disadvantage that the field of view includes a non-uniform shocked region and a curved shock front. A low intensity burst of red light was recorded at the time the first shock entered the CS$_2$, and it was followed by increasing light intensity until the shock reached the brass face at the back of the cell. At that moment the intensity decreased instead of increasing, and the later light output did not correlate well with shock events. It is not clear what happened. The observations may have been affected by

1. Microscopic bubbles of entrapped gas at the brass-CS$_2$ interface where first light was recorded.
2. Refraction of light by curved shock front may have diverted light from the field of view of the optical system and effectively obscured the source after the first short interval.
3. The decrease in intensity may be real and may indicate that the reaction is endothermic, not exothermic.
Further speculation at this point is fruitless. Another experiment is in progress which has the same geometry as the first four. The cell will be of brass, except for a sapphire back plate. There is some concern about the effect of fluorescence from the sapphire, but it will not fluoresce unless excited, and if it is excited, it will be because UV radiation from the CS$_2$ exists. So in our crude division of the spectrum we will still be able to distinguish between red and blue and measure the influence of various events on the emitted light.

IV. EXAMINATION OF SHOCK TUBE EXPERIMENTS

With the assistance of Henry Chung, who was briefly a post-doctoral student on this contract, the analysis in Reference 11 has been carefully examined for any light it may shed on reactions to be expected in liquid CS$_2$. The result has been to generate some skepticism about the validity of such experiments. There appear to be at least two questionable assumptions normally made in this type of experiment; both are implicit:

1. In the state immediately behind the shock front the gas is in thermal equilibrium and has not yet started to react.

2. The state of flow behind the shock is that of the permanent regime, i.e., each physical variable, $f$, depends on position, $x$, and time, $t$, in such a way that $f = f(x - U_5 t)$.

The first assumption is questionable because of the different relative rates at which translational, rotational and vibrational degrees of freedom come to equilibrium. The second may or may not be sound, but there is no evidence in references 9-11 that the question has been considered.

In browsing through proceedings of the 1970 Shock Tube Symposium, I see some evidence of a developing awareness of these problems at that time. An interesting fact reported by Nicholls and Pritchard is that dissociation of polyatomic molecules is first order at high pressures and second order at low pressures. The work on CS$_2$
reported in references 9-11 was carried out at low pressures - a few mm of Hg; and the authors in both cases agreed that the decomposition in liquid CS$_2$ at high pressure should be first order, but that is not strictly in accord with Sheffield's results. Some further consideration of this problem appears to be in order.

What appears to be a common error in the use of shock tubes to study gas phase kinetics turned up in the process of evaluating reference 11. It appears to be common practice to write the kinetic equation for a first-order reaction in the form

$$\frac{dn}{dt} = -k_1n$$

where $n$ is number of mols per unit volume of the species considered. A first-order reaction, as I understand it, is analogous to the decay of nuclear species. A molecule just sits around waiting for something internal to happen. When it does, it decomposes or reacts. The presence or absence of adjacent molecules has no effect on the reaction. In that case, Eq. (3) is improper in a system of changing density. Consider $N$ molecules in a volume $V$ which is changing with time. The first order reaction as I have defined it is described by the equation

$$\frac{dN}{dt} = -k_1N$$

It is perfectly proper to divide both sides of Eq. (5) by $V$, but the result is

$$\frac{1}{V} \frac{dN}{dt} = -k_1n,$$

not Eq. (4). Eq. (6) can also be written

$$\frac{dn}{dt} = -(k_1 - \frac{d \ln \rho}{dt})n$$

where $\rho$ is mass per unit volume and $V$ has been assumed to be the volume of unit mass. It is evident that if the rate of density change is of the same order as rate of
reaction, the difference between Eqs. (4) and (7) can be very significant. Whether it is in fact so for a particular experiment would require detailed examination of that experiment.

V. FUTURE PLANS

Very careful planning will be required if the absorption experiment is to succeed. A lot of time will be devoted to that and to getting the apparatus ready for the measurement.

A decision will be made soon as to whether or not the work on light emission will be pursued further. If characteristic radiation exists, it will be worthwhile. If not, the work to date will be published in a note for the benefit of other experimenters.

A great deal of time will be devoted to the questions of interpretation of spectra and the study of kinetic processes in CS$_2$. 
REFERENCES


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