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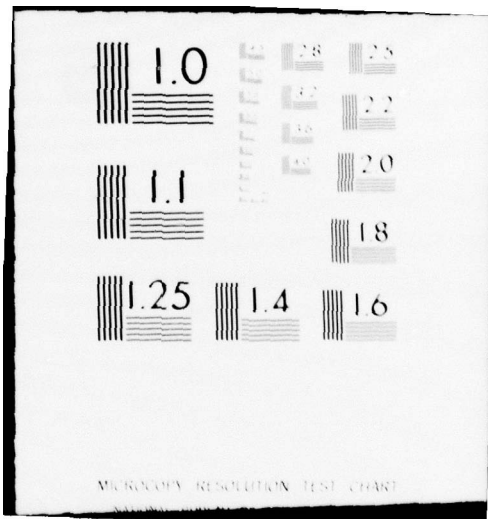
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CHEMICAL REACTIONS IN SHOCK WAVES

FINAL REPORT

W. C. GARDINER, JR.

OCTOBER 10, 1978

U. S. ARMY RESEARCH OFFICE

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18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Shock waves; high temperatures; chemical kinetics; combustion; explosions; free radicals; detonation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental and computer modeling studies were carried out on chemical reactions at high temperatures, in particular on reactions which participate in combustion processes. Reaction initiation was by shock-wave heating, and reaction progress was monitored by spectroscopic methods. Systems studied include $CS_2-O_2$ , $CH_4-O_2$ , $CH_4-Ar$ , $C_2H_2-Ar$ , $C_2H_4-Ar$ , and $C_2H_6-Ar$ .		

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## Final Report on Experimental and Modeling Studies of

### Chemical Reactions in Shock Waves

Statement of problems studied. The initial goals of this research were threefold. The first was a technical one, to explore further the use of IR laser absorption spectroscopy for the study of hydrocarbon chemistry at high temperatures. The second was to utilize this technique (together with others) to carry out experiments on important small hydrocarbon pyrolysis and oxidation mechanisms. The third was to undertake an emission spectroscopic investigation of the  $\text{CS}_2\text{-O}_2$  reaction with a view towards better understanding of the mechanism of population inversion of CO produced in the  $\text{CS}_2$  flame laser. Significant results were obtained in all three directions.

Results obtained and discussion. At the time the proposal for this grant was written, we were still engaged in theoretical research on the  $\text{CH}_4$  IR laser absorption and doing experiments on the absorptions of other hydrocarbons. The theoretical work finally led to a coherent description of the  $\text{CH}_4$  absorption as function of temperature, although the critical distinction we had hoped to be able to make with regard to line-broadening models did not materialize. As to the other hydrocarbons, as our data collection continued, our enthusiasm for getting into Zeeman tuning of the Ne or Xe laser lines diminished as our interest in utilizing the totally unexpected high absorptivities for kinetics experiments grew. The  $\text{CH}_4$  results were published in JQSRT, the results for  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$  in Applied Spectroscopy.

The essence of the implication of these results for combustion experiments is that while the lack of specificity was a disappointment, the high absorptivity for the untuned Ne line opened the door for a number of highly successful experiments. Since the writing of this proposal the advent of commercially available tunable diode lasers has rendered Zeeman-tuned rare gas lasers obsolete anyway. Therefore, to pursue the originally contemplated experiments on  $\text{CH}_2\text{O}$  and  $\text{CH}_3$  with IR laser spectroscopy would now entail adding a diode laser to our shock tube. Before undertaking such experiments, however, there are many easier ones begging to be done on the same systems.

Pyrolysis experiments have been done and published on  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . The principal techniques were laser-schlieren observations on density gradients and laser-absorption measurements on hydrocarbon disappearance. Data interpretation was done by computer modeling. While the main result in each case was the rate constant for the primary decomposition step, conclusions could also be drawn about the rate constants for important secondary reactions.

Combustion studies were also brought to the publication stage on  $\text{CH}_4$ . In the course of the data interpretation it was found that the relative lack of reactivity of  $\text{CH}_3$  radicals forces a major part of the reaction to proceed via  $\text{C}_2$ -hydrocarbon steps, particularly for rich mixtures. In order to pursue this further, a broad-scale computer modeling effort was made to determine how well a conventional methane combustion mechanism will reproduce  $\text{C}_2$ -hydrocarbon ignition data. The results indicated, primarily, that additional data is needed.

Pyrolysis experiments were also done, but not yet brought into publication form, on the pyrolysis reactions of  $\text{CH}_3\text{I}$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ . Combustion experiments upon which data analysis is still in progress are on  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ .

The final major effort on this grant concerned the oxidation of  $\text{CS}_2$ . This reaction was successfully studied using  $\text{SO}_2^+$  luminescence and unsuccessfully studied using IR thermal emission. Computer modeling of the  $\text{SO}_2^+$  results showed a good capability of the mechanism to account for ignition delays, but many basic questions about it remained unanswered. The essential problem with the IR emission experiments, which should have provided a means of probing major product species concentrations during the ignition period, was  $\text{CS}_2$  thermal emission. The broadening of the  $\text{CS}_2$   $\nu_3$  emission band at combustion temperature proved to be so great that it obscured all other emissions in the wavelength region available to us until the end of the ignition delay period. While IR ignition delay measurements were possible, the  $\text{CS}_2$  emission totally prevented attainment of the main object, exponential growth constant measurements. It will be necessary to repeat this study using a broadband IR detector.

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The following publications resulted from research carried out under this grant:

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- W. C. Gardiner, Jr., "Laser Absorption Methods for Characterizing High Temperature Gases," Characterization of High Temperature Vapors and Gases, NBS Symposium Proceedings, in press.

Appendix--Participating scientific personnel.

The following personnel participated in the research for all or part of the grant period. Degrees obtained at The University of Texas are noted by dates. Personnel with degrees from elsewhere are noted by their last university.

W. H. Brotherton  
W. C. Gardiner, Jr.  
J. H. Hardy (Ph.D. 1976)  
Y. Hidaka (Hiroshima University)  
T. Koike (Tohoku University)  
W. G. Mallard (Ph.D. 1975)  
D. B. Olson (Ph.D. 1977)  
M. H. Proffitt  
T. Tanzawa (Ph.D. 1978)  
J. N. White (B.S. 1978)