

020-3390.24-C

CHEMICAL REACTIONS IN SHOCK WAVES

FINAL REPORT

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DECEMBER 29, 1961 THROUGH OCTOBER 31, 1974

U.S. ARMY RESEARCH OFFICE

GRANT NUMBERS

DA-ARO-D-31-124-G252

DA-ARO-D-31-124-G640

DA-ARO-D-31-124-G858

DA-ARO-D-31-124-G1011

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 9 Chemical Reactions in Shock Waves, I		5. TYPE OF REPORT & PERIOD COVERED Final Report 12-29-61 through 10-31-74
7. AUTHOR(s) 10 W.C. Gardiner, Jr.		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Texas Austin, Texas 78712		8. CONTRACT OR GRANT NUMBER(s) 15 DA-ARO-D-31-124-G252 DA-ARO-D-31-124-G640 DA-ARO-D-31-124-G858 DA-ARO-D-31-124-G1011
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Research Office P.O. Box 12211, Research Triangle Park North Carolina 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 16 ARB-P-3390-C
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 14 24 Jun 1975
		13. NUMBER OF PAGES 7
		15. SECURITY CLASS. (of this report) Unclassified
		18a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited. 14 Approved for public release - 31 Oct 77!		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 15 ARB-P-3390-C		
18. SUPPLEMENTARY NOTES		
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 computational studies were carried out on a number of high-temperature chemical reactions. The experiments were done using a variety of spectroscopic techniques, coupled with shock-wave initiation of reaction. The principal results comprise mechanism explorations and determinations of elementary reaction rate constants among the reaction species H ₂ , CO, CO ₂ , O ₂ , D ₂ , C ₂ H ₂ , and CH ₄ . In the course of obtaining these results, several significant advances in the technology of shock-tube experiments and in computer simulation of reactive flow were achieved. Discoveries of particular note include coupling		

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between vibrational excitation and reaction rate for several bimolecular reactions, non-Arrhenius behavior of rate constant expressions, and participation of radical-radical processes in decomposition and isotope exchange reactions. A

Statement of problems studied. The underlying goal of all the studies carried out during the term of this project has been obtaining detailed, quantitative understanding of important high-temperature gas-phase chemical reactions. The degree to which this goal can be attained depends upon two things: the correctness and completeness of the set of elementary reactions in terms of which a given chemical process is described, and the accuracy with which one knows the rate constants of each elementary reaction. At the outset of our program, large ranges of uncertainty pervaded both aspects even for such relatively simple reaction systems such as $H_2 + O_2 \rightarrow H_2O$. As time went on, the goal of understanding simpler systems was attained to a very satisfying degree, and more complex reactions--such as $CH_4 + O_2$ --could be examined. In addition to the dominant elementary reactions, side-reactions of unusual nature, such as those leading to species in electronically excited states, were also investigated.

The reaction systems selected for study included $H_2 - O_2$; $D_2 - O_2$; $H_2 - O_2 - CO$; $H_2 - O_2 - CO_2$; $CO_2 - Ar$; $C_2H_2 - O_2$; $CH_4 - Ar$; $CH_4 - H_2 - Ar$; $CH_4 - D_2 - Ar$; $CH_4 - O_2$.

Summary of important results. A. Hydrogen-Oxygen Reaction. The $H_2 - O_2$ reaction has served the role of prototype branched-chain reaction for many years, and it was considered at the outset of our research that the principal elementary reactions and their rate constants were fairly well known for many conditions. The initial goal was thus establishing the identity and rate of the initiation reaction, through precise measurements of ignition delays. This was accomplished through the development of a very sensitive bismuth resonance lamp for absorption spectroscopic observations of OH radical. A rate constant expression for the reaction $H_2 + O_2 \rightarrow 2OH$ could be derived. In order to accomplish this, however, it was also necessary to define the high-temperature rates of the branching reactions more precisely. This turned out to require characterization not only of the exponential growth portion of the explosion, but also of the transition zone between the exponential growth and recombination zones of the explosion. These experiments, done in our laboratory and at Los Alamos, defined rate constant expressions for the branching reactions $O + H_2 \rightarrow OH + H$ and $OH + H_2 \rightarrow H_2O + H$. The transition zone reaction $OH + OH \rightarrow H_2O + O$ could also be identified and assigned a rate constant expression.

The experiments served to provide a complete description of the $H_2 - O_2$ explosion under low-pressure (< 1 atm) and high-temperature conditions. For higher pressures and lower temperatures, termolecular reactions -- $H + O_2 + M \rightarrow HO_2 + M$ and subsequent reactions of HO_2 in particular -- serve to complicate the explosion kinetics. Shock tube experiments have been done in various laboratories in attempts to explore these complications. We undertook computer simulation studies of these experiments in order to find out how much confidence can be placed in the results. It turned out, unfortunately, that non-idealities of reflected shock wave propagation affect the physical state of the shocked gas to such a degree that rate constants derived from such experiments have to be assigned large ranges of uncertainty.

The reaction between H_2 and O_2 produces only a very weak luminescence, but one that is nonetheless considered to be highly characteristic of the reaction rate. A number of elementary processes have been proposed to account for the production of the emitter OH ($^2\Sigma$). Our experiments gave strong support for the reaction $HO_2 + O \rightarrow OH^+ + O_2$ as a parallel contributor to $H + O + M \rightarrow OH^+ + M$, the reaction which has the most support from flow-tube and flame structure experiments. In addition, specific quenching of OH ($^2\Sigma$) was found to be an important contributor to the luminescence profiles in later stages of reaction. These experiments were supplemented by the D_2/O_2 analogs.

B. Carbon Monoxide-Carbon Dioxide Interconversion in Hydrogen-Containing Systems. It is well known that the so-called water gas equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ is attained primarily through the coupled pair of elementary reactions $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ and $\text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{OH}$. The rates of these two reactions were in considerable doubt until about 1970, particularly with regard to their temperature dependence. We measured the CO/CO₂ interconversion rate in both directions in the reactive environment generated by an H₂/O₂ explosion and were able to resolve the existing discrepancy in terms of rate constant expressions for these reactions which did not have the simple Arrhenius form. Theoretical studies based on collision theory and on activated complex theory confirmed the essential correctness of the non-Arrhenius forms used.

C. Exploratory Studies of Acetylene Combustion. In the early 1960's it was widely thought that straightforward extensions of the experimental methods which promised to be capable of giving full mechanistic descriptions of small-molecule reactions would be capable of giving comparably complete descriptions of combustion reactions. We devoted substantial efforts to achieving this with the C₂H₂ - O₂ reaction, accomplishing some useful data accumulation but falling far short of the goal of defining a reaction mechanism. The previously-mentioned OH-radical spectroscopic methods and the laser-schlieren technique for monitoring heat release were used to follow the main reaction, while chemiluminescence observations were made on CH*, C₂*, OH*, and CO*. The density, equivalence ratio, and temperature dependence of the observations were such that only quite rough outlines of the kinetics could be proposed. Experiments in CO and O₂ - diluents provided insight into coupling of vibrational relaxation and chemical reaction.

D. Methane Chemistry. The primary difficulty in our and others' studies of high-temperature hydrocarbon chemistry has been in developing adequate analytical techniques for the hydrocarbons themselves and radicals derived from them. A fortunate opportunity to solve this problem is the advent of tunable IR lasers. We initiated the use of IR laser absorption spectroscopy for shock tube studies of hydrocarbon chemistry by means of the coincidence absorption of the 3.39 μm Ne laser line by CH₄. Our initial results were concerned with the spectroscopy itself, viz. defining the effects of temperature and pressure-broadening upon the absorbance. We then completed studies of CH₄ pyrolysis and isotope exchange, and began studies of CH₄ oxidation. The pyrolysis experiments led to a recognition that chain reactions sustained by CH₃ radicals and H atoms dominate the CH₄ disappearance, and that $\text{CH}_4 + \text{M} = \text{CH}_3 + \text{H} + \text{M}$ serves only as an initiation reaction. The rate constants determined for the chain reactions were then used to interpret the isotope exchange experiments. While experimental studies of CH₄ oxidation did not proceed beyond the exploratory stage during the term of this project, computer simulation studies of the reaction mechanism were pursued extensively. Detailed considerations of existing shock tube data led to good understanding of the main reaction pathways and how these are manifested in experimental observations. Continuing on with our own experiments, which will combine the IR laser absorption technique with conventional spectroscopic observations, is the main pathway of our future research.

E. Computer Simulation of Reactive Flow. In the early history of shock tube research it was possible to interpret experiments using the traditional methods of data analysis of chemical kinetics. As the reactions studied became more complicated, and the precision demanded of the results improved, modern computer methods began to be applied. After a few years these methods became quite sophisticated, incorporating refined techniques of handling difficult systems of differential equations, considerations of nonideal shock propagation, and practical ways of comparing calculations with experiments. Our laboratory

has consistently been at the forefront of these developments. We contributed effective methods of setting up the differential equation integrators, procedures for taking boundary layer effects into account, procedures for determining the sensitivity of computed results to rate constant assumptions, and effective means of communicating the rationale of this type of computer study to the scientific public. A major component of this effort was the creation of a powerful computer code for numerical integration of the equations of two-dimensional nonreactive viscous flow under shock tube conditions, together with procedures for utilizing the nonreactive viscous flow results for modelling reactive flow as a variable-area equivalent core flow.

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