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EXPERIMENTAL AND MODELING STUDIES OF HIGH TEMPERATURE COMBUSTION

FINAL REPORT

W.C. GARDINER, JR.

JUNE 7, 1982

U.S. ARMY RESEARCH OFFICE

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Final Report on

Experimental and Modeling Studies of High Temperature Combustion

1. Statement of problems studied.

The goals of this research were to further our understanding of the reaction mechanisms of high temperature combustion reactions, in particular of hydrocarbons, by shock tube experiments and computer modeling. No particularly novel experimental techniques were to be used, nor were innovative types of computer modeling to be tried. Instead, the goal was to apply experimental and computer methods that had been tested in our laboratory and elsewhere to experimental situations where we expected to be able to gain worthwhile insights into the reaction mechanisms responsible for hydrocarbon flames. A portion of the experiments and computations involved the study of systems simpler than the usual fuel/oxidizer combination, namely fuels undergoing high-temperature homogeneous pyrolysis. Others were more complex than a simple fuel/oxidizer system, containing in addition to a fuel (methane) a sensitizer (higher hydrocarbon) capable of accelerating the ignition process.

2. Results obtained and discussion.

Ignition delays for shock-initiated combustion processes have proved to be very fruitful for modeling purposes in a number of previous investigations. One of the findings, supported by a broad range of modeling studies, is that there is a strong coupling between the oxidations of methane, formaldehyde, and the C_2 -hydrocarbons, due primarily to the relatively inert character of the CH_3 radical. In cross-checking the reaction mechanisms that have been used to derive rate constant expressions for the elementary reactions that are important in the ignition zone chemistry, one readily determines that a primary lack of ignition delay data taken with a consistent experimental technique for all of the stable gases concerned is impeding the progress of combustion science here. We decided that the best of the possible measures of ignition progress to use for comparing the several courses of ignition would be the refractive index change. The reason for this choice is basically that it reflects almost entirely the enthalpy production during the combustion event and is more or less blind to details of the reaction mechanism. We therefore set out to collect and interpret refractive index profiles for the ignitions of lean and stoichiometric methane/oxygen, ethane/oxygen, ethylene/oxygen, and acetylene/oxygen mixtures, each highly diluted in argon carrier gas, heated to reaction temperature in incident shock waves. The laser-schlieren equipment previously used in our laboratory for taking very short time profiles was slightly modified to extend the observation time to essentially the entire duration of the hot flow. The data proved to be very suitable for the intended purpose, and have

been subjected to intense modeling efforts with the principal result of improving the set of rate constant expressions needed to describe the key reaction pathways of the ignition zone chemistry. They will continue to be useful for this purpose, in our laboratory and elsewhere, for a number of years as reference standards. Eventually it will be possible to model not only the ignition delays of these mixtures, but also the entire refractive index profiles.

Practical fuels are usually not pure hydrocarbons, but instead mixtures of hydrocarbons often containing non-hydrocarbon species as well. Natural gas is a particular example. Depending on the source, natural gas contains varying amounts of higher hydrocarbons in addition to the main component of methane. We were drawn to consider the ignition process in natural gas from the consideration that higher hydrocarbons present as impurities may accelerate the ignition zone chemistry to a degree far in excess of their fractional content. By the study of this acceleration we hoped, and indeed showed through extensive modeling studies done before any experiments were carried out, that otherwise unattainable information about the kinetics of the ignition process could be obtained. As a practical matter, ignition of natural gas-air mixtures presents an explosion hazard that has been studied before in connection with the transition to detonation in air/natural gas mixtures resulting from accidental spills of LNG. In order to achieve the simultaneous goals of getting practically useful data as well as data useful for modeling purposes, we elected to use air in place of Ar/O_2 mixtures as oxidant and to study very fuel-lean mixtures, essentially 1% methane in air with varying amounts of other components. This study we decided to carry out not with the laser-schlieren method but rather with the more traditional diagnostics of explosion progress, namely uv and ir laser absorption, ir thermal emission, visible chemiluminescence, and pressure change. All but the latter had been used before in previous studies in our laboratory, and so there was no particular problem in adapting existing equipment for the experiments. Pressure measurements, however, were something that had never been done before in our low pressure shock tube except for shock wave arrival detection. Since we wanted to work at pressures near atmospheric, it was necessary to do a considerable amount of exploratory experiments in order to devise a mounting for the pressure transducer that would shield it adequately both from acoustic noise and from the shock-heated gas at the shock tube wall. In the final real data-taking runs, all of the diagnostics gave ignition profiles that were consistent with one another and, with the exception of the qualitative forms of the OH and ir laser absorption profiles, with the modeling calculations done in support of the experiments.

The essential conclusions of these experiments were that the sensitization of the ignition process in methane/oxygen by added hydrocarbons can be reasonably well understood in terms of reaction mechanisms and rate constants representative of the current state-of-the-art in this field. Quantitative understanding, however, can clearly not be achieved at present because, among other things, of modeling difficulties with unimolecular dissociation processes as

described later.

It has been recognized for some time that several of the rate-determining steps of hydrocarbon combustion are unimolecular reactions, and that for many conditions encountered in real-world combustion processes these unimolecular steps are in the fall-off pressure range. This implies that rate constant expressions derived from conventional experiments done at temperatures much below the combustion temperature range can be extrapolated into the range of most combustion experiments without incurring unacceptably large uncertainties from the falloff corrections employed. To come to grips with this problem we undertook two projects, one experimental and one computational. The experimental one was to measure as many of the dissociation rates themselves as we could, using the laser-absorption method, in the temperature and density range in which combustion experiments were to be done; this obviated the need for any extrapolations for the molecules concerned, and also provided tests for the theory of extrapolation as described below. The molecules concerned were methane, ethane, ethylene, propene, propane, n-butane and i-butane. Manuscripts describing the results are in part published, in part waiting on further modeling work needed to understand corrections for secondary reactions more fully.

The theoretical, more accurately computational part of the research was concerned with incorporating into our modeling programs the means to use the theory of unimolecular reactions to make as accurate estimates of the falloff corrections as can be done with present knowledge. This effort had to be rather broad in scope, as there is a considerable diversity of information available about the different unimolecular reactions that participate in combustion. For molecular dissociations whose rate constants are completely unknown, an estimate of the high-pressure limiting rate constant was made by comparison with similar reactions, and the falloff corrections were based upon the molecular geometry and vibrational frequencies. For reactions that have rate constants in the literature at some density(ies) and temperature(s), adjustments of this type of approximation were made by adopting an appropriate deactivation cross section and/or high-pressure limiting rate constant. To facilitate use by future modeling researchers, the computer codes developed were broken into two segments: one to generate the low-pressure limit rate constant as an Arrhenius expression appropriate to the temperature range under consideration, and another - within the modeling program itself - to provide the falloff corrections.

There remain to report three items of "unfinished business" that have been brought forward during this grant, but will not be reportable to the scientific community for some time. The first concerns CH_3 radical absorption spectroscopy. Our modeling research showed from early on that knowledge of CH_3 profiles would provide critical information both for decomposition and for ignition studies. We therefore set out to provide local capability to measure such profiles using the 216-nm band. This was done using two different source

lamps: a microwave discharge in flowing H_2 -He mixtures and a Zn arc lamp. The former proved to be less intense than desired (i.e. no better than previous workers had achieved using high pressure xenon lamps) and the latter had very short lifetime when operated d.c., as we feel is required for shock tube experiments. Furthermore, when used in our old rectangular shock tube, the profiles found for absorption from both lamps indicated that there were significant contributions from "junk" coming off the walls. The present status of the work is that specialized lamp-driving circuits are under construction so that we will be able to utilize the Zn lamp effectively.

The second item of unfinished business is a reservoir of data on thermal decompositions of several hydrocarbons: methane, propene, n- and i-butane. We collected a substantial amount of good laser-absorption and laser-schlieren data on these reactions, but are still blocked from publishing it because of difficulties with modeling it successfully. The essence of the matter is that with the thermochemical information that we believe to be correct and with literature data for the rate constants of secondary reactions, we are not able to give satisfactory account for the observed profiles. Something is missing from the analysis, and until we find out what it is, we have to sit on the data and wait.

The final item of unfinished business concerns remaining discrepancies in the set of hydrocarbon combustion rate constant expressions that we feel have been optimized to the fullest extent currently possible. Detailed analysis of the mechanisms and the implied matches to our own and other data shows that there is just not enough flexibility in adjusting the rate constants, or in allowing for systematic error in the experimental data, to permit matches on all fronts. Moreover, there are true differences between implications from flame modeling studies and implications from ignition experiments. It appears that some elementary chemical reactions occur in small hydrocarbon combustion that have not yet been incorporated into models. There is a clear need not so much for further modeling research as for inspiration.

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

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4. Scientific Personnel

The following persons participated in the research conducted under this grant:

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