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**SYNTHETIC FUEL COMBUSTION: POLLUTANT FORMATION. SOOT
INITIATION MECHANISMS IN BURNING AROMATICS**

First Quarterly Report for Period September 19–December 31, 1980

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SYNTHETIC FUEL COMBUSTION: POLLUTANT FORMATION.

SOOT INITIATION MECHANISMS IN BURNING AROMATICS

FIRST QUARTERLY REPORT

FOR THE PERIOD

19 SEPTEMBER 1980 - 31 DECEMBER 1980

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U. S. DEPARTMENT OF ENERGY
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ABSTRACT

Although considerable progress has been made in recent years in understanding the phenomenology of soot formation in the combustion of hydrocarbon fuels, relatively little attention has been focused upon aromatic fuels of the types commonly found in coal liquids. In particular, the effects of gas-phase free radicals, formed during combustion, on the kinetics of formation of incipient soot particles have not been characterized. Accordingly, an experimental investigation of the detailed kinetics of incipient soot formation in the combustion and pyrolysis of aromatic fuels of the benzene, anisole, phenol, and pyrrole families has been initiated in order to determine soot formation mechanisms and rate parameters. The experiments will be performed in a shock tube over the temperature range 1300-2500 K, using multiple ultraviolet, visible, and infrared diagnostics to monitor the kinetic behavior of free radicals (such as OH), incipient soot particles, and combustion products. Experiments will be conducted with artificially enhanced concentrations of free radicals such as OH and O to determine their effects on the kinetics of soot and soot precursors. The experimental work will be supported and directed by a parallel analytical effort using a detailed mechanistic model of the chemical kinetics and dynamics of the reacting systems. In this report, the design and configuration of the experimental apparatus are described, the details of the kinetic model are outlined, and possible reaction pathways are discussed.

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1. INTRODUCTION

The use of fuels with low hydrogen-to-carbon ratios and high aromatic content (such as coal liquids) in combustion systems offers the potential of substantial savings of energy and cost. However, the major difficulty in combustion of these fuels using present technology is their tendency to form soot.¹ For this reason, knowledge of the rates and mechanisms for soot formation due to pyrolysis and combustion of aromatic species commonly found in such fuels is essential to the design of new combustion systems.

Although considerable attention has been directed toward soot formation from non-aromatic hydrocarbons,^{2,3} studies of aromatic compounds are still rare, especially at high temperatures relevant to industrial combustion processes ($T \sim 1000\text{--}2000\text{ K}$)⁴. Recent Fourier-transform infrared studies of coal liquids have shown that the volatile components include alkyl-substituted aromatics, phenols, aromatic ethers, and pyrroles, as well as aliphatic species and other nitrogen heterocyclic compounds.⁵ Of these, the aromatic species whose high-temperature pyrolysis and combustion have been most commonly investigated are benzene and toluene (see, for example, Refs. 6-9). The mechanisms most commonly postulated to explain soot formation in such systems involve either polyacetylenic or polycyclic aromatic pathways. Prado et al.⁶ identified a large number of polycyclic aromatic hydrocarbons produced in turbulent benzene diffusion flames; these species, the simplest of which were indene, naphthalene, and biphenyl, were taken to be intermediates in the formation of soot. In a study of toluene pyrolysis in a Knudsen cell, Smith⁷ observed the formation of both polycyclic aromatic hydrocarbons and polyacetylenic molecules, with acetylene being the dominant pyrolysis product at temperatures above 1700 K. Similarly, Asaba and Fujii explained the kinetics of soot formation observed in shock tube studies of pyrolysis⁸ and oxidation⁹ of benzene in terms of both aromatic and acetylenic radical recombination.

In a detailed shock tube study of the pyrolysis of benzene, toluene, ethylbenzene, and indene, Graham et al.¹⁰ used a variety of scattering and absorption diagnostics to monitor the time-resolved formation of soot and its precursors as a function of temperature from 1600 K to 2300 K. The soot

yield was found to decrease dramatically with increasing temperature above 1800 K. Although no detailed kinetic or mechanistic analysis was performed, the results were qualitatively interpreted in terms of a dual-path overall mechanism which is dominated by fast "condensation" of aromatic species at temperatures below ~ 1800 K and by relatively slow polymerization and nucleation of non-aromatic fragments at higher temperatures. This interpretation was also consistent with the empirical results of Blazowski¹¹ obtained in backmixed combustion of aromatic hydrocarbons.

The majority of this literature pertains only to pyrolysis, and provides global data and characterizations of soot and soot precursors. However, in combustion processes, free radical species such as O, H, and OH may play an important role in the fragmentation of ring structures. Furthermore, fuel carbon is converted into products such as CO and CO₂. In combustion of heterocyclic species containing fuel nitrogen, NO is also formed. All of these species are amenable to detection using optical spectroscopic techniques. Thus, combustion experiments in which the temporal behavior of these radical intermediates and products is observed, together with that of both fuel and soot, should provide valuable data on the chemical pathways leading to soot formation.

The objective of this research program is to experimentally examine the effects of gas phase free radical chemistry on soot initiation times in the combustion and pyrolysis of aromatic fuels such as toluene, and to extend the data base to more complex, heterocyclic species such as pyrrole, phenol, and anisole. The experiments are to be performed in a shock tube over the approximate temperature range 1300-2500 K, with emphasis on the lower temperatures representative of industrial applications. Kinetic interpretation of the data will be carried out via computer simulation of the chemical and physical processes occurring behind the shock front. During the present reporting period, the shock tube apparatus has been assembled, several optical diagnostics have been designed, and an interpretive computer code has been made operational. In the following discussion, the experimental set-up and diagnostic designs are described in Sec. 2, and the details of the kinetic analysis and computer code are given in Sec. 3. A progress summary and plans for the next quarter are presented in Sec. 4.

2. EXPERIMENTAL

The experiments will be carried out in the shock tube apparatus shown schematically in Fig. 1. The optical and pressure observations will be made in incident shock waves at temperatures between 1300 K and 2500 K. Typical experimental conditions will employ Ar/fuel/O₂ test gas mixtures containing > 90% Ar at pre-shock pressures of ~20 torr. Attainment of the desired temperature range will require shock velocities of Mach 4-5 (1.3-1.6 km/s in Ar); the resulting test gas pressure will be 400-600 torr. These conditions can be attained using H₂ as a driver gas at pressures of 1.7-4.2 atm. Driver gas bursting pressures are controlled by selection of appropriate diaphragm thicknesses. The following sections describe the shock tube and associated gas handling lines, the calculation of the required shock conditions, the general design of the optical diagnostics, and the data acquisition system.

2.1 Shock Tube

The stainless steel shock tube¹² has a circular cross section of 10.36 cm i.d. (4.08 in) and consists of four modular sections joined by o-ring seals. The high-pressure (driver) section is 152 cm long; each of the three segments of the low-pressure (test) section is 183 cm long. The driver and test sections are separated by a diaphragm station which consists of two diaphragm holders and a plate valve. The shock waves will be initiated using the double-diaphragm technique, which assures shock reproducibility and minimizes uncertainties due to diaphragm thickness or scoring. In this method, the main driver section and the intermediate space are simultaneously filled to 100-200% and 50-100% of the single-diaphragm bursting pressure, respectively; the diaphragm rupture is then initiated by rapidly evacuating the intermediate space. The diaphragms, typically 0.2-0.5 mm thick aluminum, are prescored in a hydraulic press to ensure rapid and uniform opening times. The plate valve, located immediately downrange of the diaphragms, allows isolation of the test section during diaphragm changes, thus reducing the pumpdown time between experiments.

Fig. 1 Schematic of shock tube apparatus, illustrating some of the optical and pressure diagnostics. PMT = photomultiplier; OMA = optical multichannel analyzer (diode array + monochromator) for use in spectral surveys.

The test segment in which the measurements are made contains six observation stations spaced along the tube at intervals of 12.7 and 25.4 cm. Two of the stations contain two diametrically opposed viewing ports, while each of the remaining four stations contains four ports oriented 90° from each other, for a total of 20 observation ports. The optical measurements will be made at three four-port stations which are 12.7 cm apart; the remaining four-port station is designed for reflected shock observations and will not be used for optical measurements in these experiments. The test gas pressure before and after passage of the shock front will be monitored at each of 4-5 ports (25.4 cm intervals) by a series of piezoelectric pressure transducers (PCB Piezoelectronics, Inc. 111-A21); these measurements serve as diagnostics of shock front arrival and stability, shock velocity, test times, and shock attenuation effects. Windows and pressure gauges are affixed to the observation ports by means of bored-out brass plugs, with o-ring seals, which are clamped onto each port; these plugs are designed to facilitate window cleaning and replacement, and are carefully machined in order to minimize protuberances beyond the i.d. of the shock tube.

High pressure hydrogen gas is introduced to the driver and diaphragm sections via a remotely operated stainless steel manifold; these sections are exhausted through a 2000 l dump tank/forepump combination. Test gas mixtures, containing at least 90% Ar and a few per cent aromatic fuel (vapor phase) and O₂, will be prepared and stored in a 90 l stainless steel mixing chamber connected to the test section of the shock tube; the test section and mixing manifold will be evacuated through a liquid-nitrogen-baffled oil diffusion pump. The mixing manifold and test section will be wrapped with heating tape and insulated to allow heating of the walls to 50-100°C when necessary to prevent fuel condensation; however, for most of the fuels under consideration, the vapor pressure at room temperature is sufficient for these experiments.

A preliminary stress analysis on the shock tube apparatus indicates that the portion to be subjected to the shock events can withstand a dead load of ~ 100 atm with a safety factor of 3.5. Several redundant pressure

regulators and safety relief valves will be used to protect the system to less than 10 atm, which is the upper limit to be encountered in these experiments. The aromatic fuels will be stored in flame proof cabinets and transferred in a fume hood using standard safety techniques, and all gases from the shock tube vacuum system will be exhausted directly through a blower in the roof. Spontaneous detonation of either the fill or exhaust gas mixtures is highly unlikely near room temperature; in any case, the pressure change in such an event would be negligible due to the limited amounts of fuel and oxygen available.

During the present reporting period, the basic shock tube has been cleaned, mounted on stands, and assembled. The observation segment was modified by adding six new ports (of the twenty now available) and remachining the original ports to improved tolerances. The high-pressure driver gas manifold and control panel were designed and constructed. The diaphragm holder/plate valve assembly and test gas mixing manifold were also designed and are now in fabrication. The remaining vacuum system assembly will be completed early in the next quarter.

2.2 Calculation of Required Shock Conditions

Detailed methods for computing shock wave parameters from Rankine-Hugoniot relations are given in a number of sources,^{13,14} and will only be briefly summarized here. When the diaphragms rupture, the high pressure driver gas acts essentially as a piston and drives a shock wave ahead of itself into the test gas. The relationship between the incident shock front, the test-driver gas contact surface, and the opposing rarefaction wave is shown in Fig. 2. Here the physical states of the unshocked test gas, the shocked test gas, the expanding driver gas, and the unexpanded driver gas are denoted by the subscripts 1, 2, 3, and 4, respectively. The experimental parameters of interest are: the Mach number M_1 of the incident shock (ratio of shock speed to test gas sound speed); the ratio of post-shock and pre-shock test gas temperatures T_2/T_1 ; and the pressure ratio P_4/P_1 (across the diaphragm) which must be used to achieve the desired T_2 . For an ideal gas (or an inert monatomic gas below ~ 8000 K), these quantities are related as follows:

Fig. 2 Diagram of axial position x along shock tube vs. time t ; the diaphragm is located at $x = 0$, the end wall of the driver section is at $-x = \chi_4$, and observations are made behind the incident wave at $x > 0$. The reflected rarefaction head overtakes the contact surface at the point (χ_c, τ_c) , thus determining the maximum test time $\Delta\tau$.

$$\frac{T_2}{T_1} = \frac{\left(\gamma_1 M_1^2 - \frac{\gamma_1 - 1}{2}\right) \left(\frac{\gamma_1 - 1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma_1 + 1}{2}\right)^2 M_1^2} \quad (1)$$

$$\frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left\{ 1 - \frac{\gamma_4 - 1}{\gamma_1 + 1} \cdot \frac{a_1}{a_4} \left(M_1 - \frac{1}{M_1}\right) \right\}^{-\left(\frac{2\gamma_4}{\gamma_4 - 1}\right)} \quad (2)$$

where a_n and γ_n denote the sound speed and specific heat ratio C_p/C_v for the gas in region n . In order to map the shock velocities and driver pressures required to cover the desired temperature range, Eqs. (1) and (2) were applied to the case of H_2 driver and Ar test gas; the results of these calculations are given in Figs. 3 and 4. The initial temperature T_1 is 300 K for most cases; initial pressures will be in the 10-30 torr range. It can be seen that driver pressures of 1-5 atm are required to cover the temperature range of interest. In the actual experiments, the shock velocity is determined from the pressure transducer shock arrival data, and the temperature behind the incident shock (prior to chemical reaction) is calculated from the Rankine-Hugoniot equation using real gas thermodynamic properties for the actual test gas mixture. The true gas temperature may deviate slightly from the no-reaction temperature due to shock attenuation or instability (which can be qualified with the shock arrival measurements), boundary layer growth along the walls, or heat release from chemical reactions; these effects can be taken into account in the numerical simulations of the chemistry and dynamics of the shocked gas, as described in Sec. 3.

From the (x,t) diagram in Fig. 2, it can be seen that, at some point (χ_c, τ_c) downrange of the point of shock initiation, the reflected rarefaction wave overtakes the contact surface to give a maximum high-temperature test time $\Delta\tau$. For ideal shock/ideal gas conditions, these quantities are related by:

Fig. 3 Incident and reflected shock velocities required for H_2 driving Ar, 1500-2500 K.

Fig. 4 Performance map of pressure behind incident and reflected shock and static driver load required for H_2 driving 30 torr Ar, 1500-2500 K.

$$\tau_c = \frac{2\chi_4}{a_4} \left\{ 1 - \frac{\gamma_4 - 1}{\gamma_1 + 1} \cdot \frac{a_1}{a_4} \left(\frac{M_1^2 - 1}{M_1} \right) \right\} - \left(\frac{\gamma_4 + 1}{2(\gamma_4 - 1)} \right) \quad (3)$$

$$\chi_c = \tau_c \left\{ \frac{2a_1 (M_1^2 - 1)}{(\gamma_1 + 1) M_1} \right\} \quad (4)$$

$$\Delta\tau = \tau_c \left\{ 1 - \frac{2(M_1^2 - 1)}{(\gamma_1 + 1) M_1^2} \right\} \quad (5)$$

where χ_4 is the length of the driver section and the other quantities are defined as before. Equations (3)-(5) predict maximum test times of $\sim 700 \mu s$, which occur at a point ~ 1.7 m downrange of the diaphragm station. However, since these calculations are subject to the non-idealities outlined above, these results will be verified experimentally with a series of test shocks into argon; the test times can be increased if necessary by simply using a longer driver section.

2.3 Optical Diagnostics

The availability of several optical ports and data acquisition channels allows simultaneous detection of reactant, intermediate, and product species by accepted spectroscopic emission and absorption techniques. Species such as the parent fuel, OH, O, NO, CO, CO₂, and soot will be monitored in the ultraviolet, visible, and infrared. These diagnostics are now in the design stage and will be completed during the next quarter.

Parent fuel compounds will be observed by UV absorption near 300 nm,^{8,9} using a continuum light source and filtered photomultiplier tube; alternatively, the fuels can be monitored in emission near 3.3 μm ,¹⁵ using a filtered InSb detector. Both methods are subject to the problem of non-specificity, since it seems likely that the aromatic radicals which are formed during pyrolysis or combustion would possess spectral signatures similar to those of the parent compound. However, these measurements should be specific to

the removal of the parent species at early times, before the radical concentrations become large enough to interfere.

The concentration of OH radicals will be determined by resonance absorption at 309 nm. OH resonance radiation will be produced by microwave discharge of a flowing mixture of H_2O and Ar after the method of Kaufman and coworkers,¹⁶ and will be directed across the shock tube diameter through sapphire windows; the transmitted radiation will be observed by a monochromator (Spex, 1.25 m) and photomultiplier tube. Care must be taken to eliminate interference from emission in the shock tube; this can be done either by using simultaneous monitors of emission and transmitted resonance radiation, or, more simply, by limiting the collection efficiency of the monochromator. The absorption data will be analyzed in terms of the standard resonance radiation formulae¹⁷ using Voigt absorber line profiles and the spectroscopic data tabulated by Learner¹⁸ and Dieke and Crosswhite¹⁹; the absorption model will be verified by calibration shocks of $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures under conditions where [OH] achieves a steady state level which can be calculated from well-known kinetic rate parameters.^{20,21} Preliminary estimates indicate that OH concentrations as low as 10^{13} molecules cm^{-3} can be determined by this method.

Atomic oxygen can be monitored by two complementary techniques. Absolute concentrations of O can be determined by resonance absorption at 130 nm, using a discharge-flow line source²² and a filtered photomultiplier with a salicylate-coated window. Again, the absorption can be modeled as for OH; however, calibrations using the well-known²³ N_2O thermal dissociation process, as used by other investigators,²⁴ should be straightforward. Preliminary estimates indicate a sensitivity of $\sim 10^{10}$ molecules cm^{-3} using this method. However, the technique may be compromised in some experiments by O_2 and hydrocarbon absorption or by the presence of large O concentrations extinguishing the line. An alternative method for observing relative O concentration in combustion mixtures is by observing the emission from the CO-O flame spectrum near 435 nm with a filtered photomultiplier, where CO is either formed as a combustion product or is added to the test gas mixture.²⁵⁻²⁷ Since the observed flame intensity is proportional to the product [CO][O], simultaneous data on the behavior of [CO] from infrared emission measurements (see below) can be used to deduce time profiles of relative [O].

Similarly, incipient soot concentrations can be detected by complementary attenuation and emission techniques. In the former case, soot is detected by attenuation of a He-Ne laser beam at 633 nm using a narrow-band filter and photomultiplier; this technique has been applied to shock-heated aliphatic²⁸ and aromatic¹⁰ hydrocarbon mixtures. The incipient soot particles (~ 10-30 nm in diameter) may be assumed to attenuate light according to the small particle limit of Mie theory²⁹; this results in a Beer's-law-type relationship between absorptivity and soot concentration. Although the effective absorption coefficient is commonly assumed to be independent of temperature,¹⁰ it is in principal weakly temperature-dependent through the refractive index of soot (which is, unfortunately, not well characterized). Preliminary estimates, approximating soot as graphitic carbon and using the refractive index data of Dalzell and Sarofim,³⁰ indicate a detection threshold of $\sim 10^{-8} \text{ g cm}^{-3}$ ($[C] \sim 5 \times 10^{14} \text{ atoms cm}^{-3}$) using the attenuation method. By contrast, the intensity of visible/infrared emission from incipient soot particles can also be represented in the small particle limit, and is strongly temperature- and wavelength-dependent through the blackbody function. This opens the possibility of determining the particle temperature by means of simultaneous measurements at more than one wavelength.

A number of other species will be monitored where appropriate. For example, in heterocyclic experiments, NO can be observed by resonance absorption near 230 nm, using the same optical system as for OH except with a trace of $\text{N}_2 + \text{O}_2$ in the discharge lamp instead of H_2O . CO_2 and CO will be observed by infrared emission at 4.3 and 4.7 μm , respectively, using bandpass filters and liquid-nitrogen-cooled InSb detectors. In many experiments, it will also be desirable to observe emission from the C-H stretching mode of the parent fuel, as discussed above; these bands occur in the vicinity of 3 μm , as do similar bands for N-H and O-H stretches in organic species.³¹ All of these infrared features have been observed in similar shock tube experiments on hydrocarbon combustion.³²

All of the above spectral diagnostics are subject to interference due to molecular emission/absorption bands of other species formed during the reactions. These bands could be sharply defined systems such as those of

CH(430 nm) or C₂(500 nm, Swan bands). However, much greater potential interference could arise from large hydrocarbon radicals and/or soot precursors, which can be expected to exhibit quasi-continuum spectra at these temperatures; indeed, inspection of the data of Refs. 10 and 28 suggests the presence of such effects in the measurements. In traditional shock tube experiments, such spectral signatures are extremely difficult to characterize in any detail. In our experiments, emission and absorption features present in the shock-heated gas will be qualitatively characterized by a limited series of spectral surveys; a Reticon diode array system coupled to a Jarrell-Ash 0.275 m scanning monochromator will provide single-shot coverage of the visible and near UV with $\sim 5 \text{ \AA}$ resolution. These surveys will serve not only to characterize the spectral backgrounds near wavelengths of interest, but also to identify additional spectral features which might warrant more detailed, time-resolved measurements.

2.4 Data Acquisition

Primary data acquisition is carried out via a CAMAC crate and branch driver interfaced to an in-house Prime 400 computer system. Pressure transducer and photometric data are fed through low-noise differential amplifiers into a multichannel digitizer/memory system; two digitizers (LeCroy 8210) and memory modules (LeCroy 8800/10) provide a total of 8 10-bit data channels and 64 K of memory with data rates up to 1 MHz. After each shock wave experiment, the data are transferred from CAMAC to the computer for disc storage and/or permanent storage on magnetic tape. The software for transferring and displaying the data is essentially complete; FORTRAN programming for data reduction and analysis will be initiated during the next quarter.

3. INTERPRETIVE KINETICS CODE

The interpretation of fundamental kinetic data in complicated chemical systems such as the combustion and pyrolysis of hydrocarbons requires the construction of a detailed kinetics model with which to simulate the experimental results. Such a model contains a mechanism consisting of as many as 50-100 elementary reactions, each of which requires specification of reactants, products, thermochemistry, and rate constants as functions of temperature. The rate law for such a mechanism consists of a set of coupled differential equations which must be integrated numerically; however, the computations are often difficult in combustion systems due to large, rapid excursions in the rates of many of the free radical reactions ("stiffness").

We have adapted a shock wave/kinetics code generously provided by Prof. W. C. Gardiner, Jr. of the University of Texas at Austin. This code uses Gear's numerical integration algorithm³³ to solve the set of differential equations describing the chemical kinetics and steady, variable-area, inviscid, compressible flow for incident shock waves; constant density conditions are used for reflected shocks. This code and earlier versions have been applied by Gardiner and coworkers to a multitude of shock wave kinetics problems for over a decade (see, for example, Refs. 21, 26, 28, 34, and references cited therein). In this section, we describe the numerical approach, the methods for dealing with boundary layer effects, and the general form of the reaction mechanisms to be used in the analysis.

3.1 Numerical Relationships

In general, a reaction mechanism consists of a set of reactions of the form

where each reaction may be an elementary molecular process or may represent some net conversion (for some atom and radical recombination processes, it

is often necessary to introduce a general third body to allow for collisional stabilization of the product). Here the stoichiometric coefficients are a , b , c , and d ; the forward and reverse rate coefficients are k and k_- , respectively, and are related to each other through the equilibrium constant (detailed balancing):

$$K_{eq} = \frac{k}{k_-} \quad (7)$$

The net reaction rate is given by

$$\begin{aligned} -\frac{1}{a} \frac{d[A]}{dt} &= -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \\ &= k[A]^a[B]^b - k_-[C]^c[D]^d \end{aligned} \quad (8)$$

Thus, for a set of S species and R reactions, we can write S differential equations, each of which describes the net formation or destruction rate of one of the species. The reaction time t is related to the distance x behind the shock front through U_2 , the gas flow velocity out of the shock front (i.e., $U_2 = dx/dt$). These equations are further coupled to equations describing the conservation of mass, momentum, and energy across the shock to give a set of $S + 3$ simultaneous first order differential equations in the $S + 3$ unknowns $\{C_j\}$, T_2 , P_2 , U_2 , where C_j is the concentration of species j . These equations are solved numerically as a function of time by starting at the shock front with the initial $\{C_j\}$ of the hot test gas and with T_2 , P_2 , and U_2 as computed from the no-reaction, real gas formulae outlined in Sec. 2.2, and incrementing stepwise along the time or distance coordinate.

For most high-temperature chemical systems, the rate equations exhibit the property known as "stiffness"; this means that, due to time constants in the solutions which vary over many orders of magnitude, there exist regions of the integration where the first derivatives are small differences between two large numbers. This is typical of species which react as rapidly as they are

formed, such as free radicals in a gas. For most numerical integration procedures, this condition necessitates prohibitively small step size. To circumvent this difficulty, the code used here employs the integration algorithm developed by Gear,³³ which is an implicit method for efficiently solving stiff systems of differential equations.

As input for the calculations, the mechanism is specified as a set of chemical reactions and expressions for the forward rate coefficients as functions of temperature. The reverse rate coefficients are computed at each step from the equilibrium constants, which in turn are computed from thermodynamic data, using polynomial representations of tables of heat capacity, free energy, and enthalpy as functions of temperature. The thermodynamic data are obtained from JANAF tables³⁵ where possible; however, data for aromatic species must be obtained from other sources³⁶ or, in some cases, must be estimated by empirical methods.³⁷

The calculations are performed on an in-house Prime 400 computer. The results of a trial calculation for propane pyrolysis are shown in Fig. 5; the trial mechanism used in this calculation contained 17 species and 44 reactions describing the pyrolysis of propane and lower hydrocarbons.

3.2 Corrections for Boundary Layer Effects

The development of boundary layer flow along the walls of the shock tube can have three types of effects upon the interpretation of the experimental data; these effects are especially pronounced at late times. First, the flow of mass into the cold boundary layer affects the flow properties in the hot core gas. Second, the buildup of a sufficiently thick boundary layer can interfere with optical measurements of the hot gas. Third, the boundary layer undergoes a transition from laminar to turbulent flow at late times, often limiting the useful test time.

For our experimental conditions, the first two effects are small perturbations and the numerical simulations can be corrected for their effects using widely accepted analytical formulae.³⁸ The flow effects are accounted for by a variable-area fluid dynamic model; the boundary layer thickness, which varies inversely as $P_1^{1/2}$, is estimated from the maps of

Fig. 5 Sample predictions of kinetics code for pyrolysis of propane (C_3H_8) at $T_2 = 1650$ K. Test gas is $C_3H_8/Ar = 0.04/0.96$ at $P_1 = 20$ torr.

Ref. 38 to be less than 0.3mm for the available test times, resulting in a 0.5% effect on the absorption measurements. However, it should be noted that the formulae of Ref. 38 are analytical approximations, and more precise corrections can be derived from numerical solution of the viscous flow equations for the actual experimental conditions.³⁹

The laminar-turbulent transition point is best characterized experimentally.³⁸ The flow time at which this occurs varies inversely with P_1 and is highly dependent on properties of the individual shock tube such as surface roughness or diaphragm rupture; from the maps in Ref. 38 and measurements in other shock tubes,⁴⁰ this time could be a few hundred μ s and thus shorter than the maximum rarefaction-limited test time discussed in Sec. 2.2. The boundary layer flow can be characterized experimentally using thin-film-resistor heat transfer gauges mounted flush with the shock tube walls^{38,40}; the onset of turbulence in the boundary layer causes a characteristic sharp increase in the rate of heat transfer to the thin-film resistor. These measurements will be performed during the tube performance tests in the next quarter.

3.3 Example Chemical Mechanisms

The analytical approach will begin with the assembly of feasible pyrolysis/oxidation mechanisms for benzene and toluene using information available in the literature. Each mechanism must contain elementary reactions describing the important phases of the overall process, e.g., ignition, chain branching, recombination, and incipient soot formation. (It should be noted that, since the major program objectives deal with the events leading up to soot formation, heterogeneous reactions involving the soot phase will not be quantitatively addressed here.) This initial model will then be used to locate problem areas in the rate information and to determine ranges of experimental conditions and data parameterizations which will provide maximum sensitivity to the processes in question. The model will then be developed to its optimum level of sophistication by iterative comparisons between simulated and observed results. In order to quantify these comparisons, the observed kinetic data will be parameterized in terms of induction times, appearance/disappearance rates, plateau or peak values, etc., as functions of temperature; these can be directly compared to the analogous parameters

predicted by the model. Since the observed species will include reactants, radical intermediates, and products, each measurement will probe a different portion of the overall set of reactions.

A limited amount of mechanistic information is available from previous studies of pyrolysis and combustion of benzene and toluene. Fujii and Asaba^{8,9} monitored benzene conversion and proposed chain mechanisms for pyrolysis and combustion; McLain et al.⁴¹ adapted those mechanisms to model their observations of CO and CO₂ formation in benzene and toluene oxidation. Trial mechanisms for benzene and toluene oxidation, based on the work of Refs. 8, 9, and 41, are shown schematically in Figs. 6 and 7, with emphasis on the overall reaction pathways. In general, the aromatic rings either fragment due to pyrolysis and/or free radical attack, or combine to form more condensed ring structures.

As discussed in Sec. 1, the relative contributions of these two pathways to soot formation are still somewhat controversial. The work of Graham et al.¹⁰ using optical soot diagnostics indicates high soot yields apparently due to ring condensation, and measurements of flame effluents⁶ show the presence of condensed ring structures; however, recent studies of toluene pyrolysis using mass spectroscopy^{7,42} indicate that the fragmentation pathway is dominant.

Kinetic modeling calculations may help to illuminate this issue. In the postulation of a reasonable $C_i \rightarrow C_{i+2}$ growth mechanism for soot precursors, it is important to establish its feasibility from the standpoint of unimolecular reaction rate theory. The existence of such a mechanism would imply that a given C_i species is relatively stable against unimolecular decomposition; this in turn must suggest some trends in thermodynamic properties of C_i such as binding energy and/or structure. This point will necessarily be addressed during development of the kinetic model.

While the kinetics of pyrolysis and oxidation of the aliphatic ring fragments are relatively well studied, very little information exists on rate coefficients for processes involving aromatic parent fuels and radicals. The measurements of Refs. 8, 9, and 41 primarily probe the initiation reactions, i.e., those which most directly affect the utilization of the parent

Fig. 6 Possible mechanism for oxidation of benzene.

fuel; these results serve as a starting point for the calculations. In our experiments, the various species measurements will be sensitive to a range of reaction types. The kinetic model can be used to map the sensitivity of each measurement to a given reaction (or set of reactions) by assessing the effects of systematic variation of rate parameters upon the predicted concentration profiles.⁴³ For example, measurements of [OH] in toluene combustion of a given fuel/O₂ mixture may be sensitive to radical initiation rates at early times, chain branching rates (e.g., O + C₇H₈ and OH + C₇H₈) at intermediate times, and radical recombination rates at late times. In experiments planned for the second year of this program, radicals such as OH and O will be "seeded" into the reacting mixtures via thermal decomposition of parent compounds; these experiments will thus provide data which are highly specific to rates of reactions between the seeded radical and both the parent fuel and its primary aromatic radicals. In this way a more complete kinetic data base can be developed which will allow improved predictive value in models of pollutant formation in combusting aromatic mixtures.

4. PROGRESS SUMMARY AND RESEARCH PLANS

The design and assembly of the shock tube apparatus and gas handling systems are ~ 90% complete; the remaining components, a diaphragm holder assembly and test gas mixing system, are nearing completion. Basic shock calculations have been performed to map the desired experimental conditions, and a safety analysis of all phases of the experiment has been carried out. Initial optical diagnostic concepts and data acquisition methods have been defined, and most of the associated equipment has been acquired. A kinetics shock computer code has been acquired, adapted, and exercised for a test case. A comprehensive survey of the literature on hydrocarbon combustion has been conducted, and available kinetic and thermodynamic data related to aromatic species have been acquired; this literature collection will continue to be supplemented throughout the program.

Plans for the coming quarter are oriented primarily toward bringing the shock tube facility to full operational status, in accordance with the program schedule. Following completion of the remaining assembly, a series of $H_2 \rightarrow Ar$ test shocks will be fired in order to determine performance characteristics such as position of maximum test time, boundary layer growth, and shock wave attenuation and wobble; the results of these tests will be used to define the final experimental configuration. The detailed designs of the optical diagnostics and associated electronics will be completed, and final set-up and calibration shocks will be initiated. The data acquisition system will be operated, and initial routines for data processing and reduction will be prepared. Some initial experiments involving aromatic species are also anticipated. The available kinetic and thermodynamic data will be used in the kinetics code to perform trial calculations of possible concentration profiles; comparisons to measurements of other workers will be made if appropriate.

The program accomplishments to date are reasonably consistent with the original program schedule, and no major difficulties have been encountered. Contributing technical personnel have been and will continue to be W. T. Rawlins, T. Tanzawa, R. H. Krech, S. Schertzer, and J. F. Cronin.

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