MODULATED MOLECULAR BEAM MASS SPECTROMETRIC STUDIES
OF THE HIGH TEMPERATURE PYROLYSIS OF HYDROCARBONS

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INTRODUCTION

The high temperature chemistry of hydrocarbons is an important field of research due to the relevance to a number of areas of energy production as well as the environmental impact of these energy sources. The complex chemistry of hydrocarbons at high temperatures is of vital importance to combustion, high temperature pyrolysis, and conversion processes. The formation of carbon or particulate matter in hydrocarbon-rich high temperature systems also appears to be controlled by these processes. While it is known that a large suite of aromatic hydrocarbons are formed directly from complex fuels such as coal, they are also known to result from gas phase reactions of much simpler fuels under turbulent combustion conditions. Indeed, there has been much discussion in the literature on the roles of various organic radicals, polycyclic aromatic hydrocarbons, and polyacetylenes as probable precursors to soot formation. (See for example References 1-6.)

While the importance of the intermediates, reactions, and products of the high-temperature pyrolysis of fuels is obvious, there have been relatively few studies of such high-temperature (>1200°C) pyrolyses. Additionally, very few studies have involved fuels more complex than methane[7] and acetylene[8]. The reasons for the paucity of data are related to the technical problems in carrying out such pyrolyses at high temperature in a meaningful manner, and the requirement of universal detection for a variety of unstable and stable molecules.

Modulated molecular beam mass spectrometric methods are uniquely suited for such measurements of high temperature vapors. Radicals and other reactive species can be detected with as nearly equal ease as stable compounds. The techniques of low energy electron impact and phase angle spectrometry allow one to determine the molecular weight of most species in even relatively complex mixtures. The chemical processes in the reaction cell can be observed as a function of temperature and/or pressure to determine first order and second order rate data. Additionally, many details of the reaction mechanism can be unravelled using appropriately labelled isotopic compounds. The combination of these techniques provides a powerful tool for the investigation of aromatic hydrocarbon chemistry at high temperatures.

EXPERIMENTAL

Figure 1 gives a schematic illustration of the high-temperature furnace-modulated molecular beam mass spectrometer used in this work. The high-temperature furnace is capable of heating a Knudsen cell to temperatures of 3000°C. The gas inlet consists of a 0.16 cm I.D. tube, press fit into the cap of the tungsten Knudsen cell and a Swagelok connection to the gas inlet line outside the high-temperature zone.

The temperature of the radiatively-heated Knudsen cell is monitored using thermocouples, optical pyrometry, and a Hall Effect watt transducer. The temperature may be set manually or programmed remotely. Species flowing from the Knudsen cell pass through a series of holes in the heating element, heat shields, and cooling jacket. A pressure of 10^{-7} to 10^{-3} torr, depending upon the pressure in the Knudsen cell, is maintained in the high-temperature furnace region using a turbomolecular pump. The entire high-temperature furnace assembly may be moved in a plane perpendicular to the molecular beam, using a set of micro slides, to allow precise positioning of the furnace relative to the molecular beam skimmer (used for beam collimation). The molecular beam is modulated using a rotating toothed wheel and passes through a mass spectrometer ion source. Modulation of the beam allows the complete elimination of background species from the mass spectra.

The modulated beam is analyzed using one of two interchangeable Extranuclear quadrupole mass spectrometers. For highest sensitivity, the axially mounted mass spectrometer may be positioned within 1.5 cm of the chamber divider (or approximately 7 cm from the Knudsen cell). This mass spectrometer may also be moved back approximately 15 cm to allow the application of phase angle spectrometry (Figure 1). In phase angle spectrometry, the phase shifts resulting from the mass-dependent flight times of molecular species between the chopper and ionizer allow one to determine the molecular weight (often to ±5%) after calibration with known species. Alternatively, the molecular beam may be analyzed using a second mass spectrometer operated in the crossed-beam mode (Figure 1); this has the advantage of a greatly reduced noise level at high temperatures. Additional details of the experimental arrangement have been published.[9]

ANALYSIS OF MASS SPECTROMETRIC DATA

To identify and determine the relative concentrations of the various hydrocarbon species is a complex task requiring a combination of mass spectrometric techniques. The primary problem which has to be overcome in obtaining concentration profiles is distinguishing parent ions of the various pyrolysis products from ions formed by fragmentation of larger species, particularly those fragment ions of the molecular ion. Mass spectra of the products of hydrocarbon pyrolysis are typically recorded at several different electron energies (e.g., 10, 12, 14, 15, 17, and 25 eV) at small pressure increments, and at small temperature increments while slowly heating the reaction cell for both the tungsten and quartz cells. An example of the raw data obtained for pyrolysis of benzene at 10^{-3} torr in a 3 mm orifice Knudsen cell using 15 eV electrons is illustrated in Figure 2. At 1200°C, C_6H_6 accounts for nearly 98% of the total phase sensitive signal (from the lock-in amplifier). Over a period of about 40 min, the temperature was ramped to 1900°C. Above 1200°C pyrolysis of the benzene molecule becomes important and C_4H_2 and C_2H_2 neutral products are detected readily as their molecular ions (Figure 2). One should note that the raw data given in Figure 2 is normalized and excludes the correction for a background of benzene which becomes substantial in the furnace chamber resulting in a small modulated component even at temperatures where the benzene is essentially totally pyrolyzed in the cell (>1840°C). A correction for this background signal is simple, and at low electron energies, is necessary only for the molecular ion.

The addition of computer control of the mass spectrometer and computerized data acquisition and handling has greatly enhanced practical capabilities of the apparatus while greatly reducing analysis time. For example, data similar to that presented in Figure 2 can be generated for all products of benzene pyrolysis. The total experiment time is less than 1 hour. Similar reductions in analysis time are noted in the calibration experiments, appearance potential measurements, and treatment of the data to extract kinetic information.

Since many of the products of hydrocarbon pyrolysis coincide with fragment ions of the molecular ion, a methodology had to be developed to distinguish parent and fragment ions. The fragmentation pattern for most hydro-

-3-

carbons, in contrast to the assumption commonly employed in high-temperature mass spectrometry, was found to be highly temperature dependent. For example, for toluene at room temperature, the only detectable fragment ion at 17 eV is $C_7H_7^+$. However, at 1200°C, $C_3H_3^+$, $C_4H_4^+$, $C_5H_5^+$, and $C_7H_6^+$ fragment ions are also observed in abundances comparable to ions resulting from the corresponding neutral species.

To resolve this problem, it is necessary to work at sufficiently low electron energies to avoid contributions by fragmentation to a given m/e ratio, while maintaining an electron energy sufficiently high to obtain the desired sensitivity. The most useful tool in this regard is phase angle spectrometry, which allowed an unambiguous determination of the molecular weight (to ±5%) of the neutral precursor of a given ion (in the effusive flow range). For cases where the resolution of phase angle spectrometry is insufficient to resolve parent and fragment ions (e.g., $C_4H_3^+$ from C_4H_3 or C_4H_4, or $C_7H_7^+$ from C_7H_7 or C_7H_8 for toluene), it is necessary to rely on the behavior of the relative ion intensities as a function of electron energy.

The measurement of appearance potentials (A.P.'s) for various species in the high temperature spectra also aids interpretation. These measurements, however, must be used with care since different methods of data analysis (e.g., the extrapolated voltage difference, linear or semilogarithmic methods, etc.) may give different results. These differences may result from a combination of factors which include the convolution of A.P. curves from both parent and fragment ions, the possibility of unsuspected radicals and isomeric structures at high temperatures, and the increased size of the A.P. curve's thermal "foot" near threshold at increased temperatures. A typical set of results for A.P. measurements as a function of temperature using the linear extrapolation method are given in Figure 3. This figure gives the A.P.'s for $C_7H_7^+$ and $C_7H_8^+$ in toluene. The results for the $C_7H_8^+$ molecular ion remain reliable whereas the results for the $C_7H_7^+$ species reflect the various contributions discussed above. These results, however, do provide clear support for the existence of a C_7H_7 radical at temperatures above 900°C in toluene. Good agreement (to ±0.5 eV) with literature values is usually obtained in the absence of these problems.

The relative concentrations obtained as described above must then be corrected for ionization, transmission, and detection efficiency at the ap-
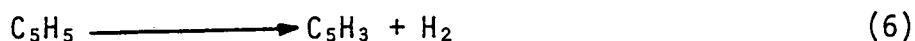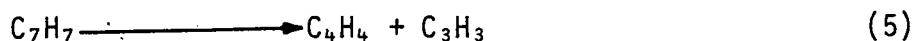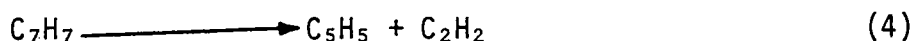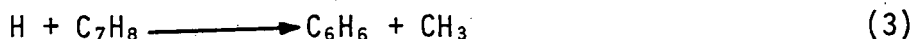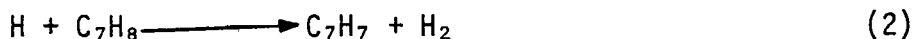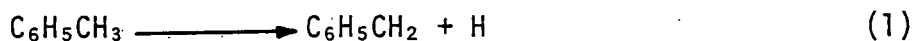
propriate temperature, pressure, and electron energy. Direct calibration is possible in some cases; however, one must ultimately resort to empirical methods or estimated values for these corrections in the case of most radicals. In these cases, calibration has utilized compounds having a (hopefully) similar structure (or at least molecular weights) and ionization cross sections. For example, C_6H_6 was used for C_6H_5, and C_3H_4 for C_3H_3 calibration. Ionization and transmission efficiency of the high-temperature species and the calibration compound are typically measured, under similar conditions if possible, at 2 or 3 eV above the measured appearance potential. In this manner it is believed that the relative concentration of species in the high temperature region can be determined with an uncertainty of less than ±30%. Relative concentrations as a function of temperature are believed to be good to better than ±10%, since these data are derived directly from relative ion currents.

Comparison of results for tungsten and quartz Knudsen cells with 2 mm diameter orifices have shown only very minor differences in the observed concentrations. C_6H_6 did seem to be produced from toluene in greater concentrations in the tungsten cell (by a factor of about 1.5); however, the minor differences appear not to suggest contributions due to heterogeneous catalysis. Measurements of the unimolecular rate constants in both cells show no differences outside of experimental scatter. Additionally, there is little evidence of darkening or surface deposits in the cells even after many hours of operation at high temperatures and pressures of 10^{-2} torr for most compounds. Also, the formation of a surface deposit by pyrolysis (of benzene or isopropyl iodide) did not affect product distributions or reaction rates. (The formation of a black "sooty" film was observed on and around the beam skimmer for all high-temperature experiments, suggesting the polymerization of reactive species on the cool surfaces.) Collectively, these observations suggest that the nature of the surface is not important in the high-temperature pyrolysis of aromatic hydrocarbons. Other workers have suggested that catalysis is rarely important under the conditions of high temperatures and low pressure.[10]

RESULTS AND DISCUSSION

The concentrations of the major products (excluding H_2 and H in the pyrolysis of toluene) as a function of temperature at approximately 10^{-2} torr total pressure are given in Figure 4. Figures 5 and 6 give the concentrations of several of the major pyrolysis products as a function of pressure at 1280°C. In these figures, the arbitrary pressure scale ranges from, and is proportional to, approximately 10^{-5} to 10^{-4} torr at the low pressure to approximately 10^{-2} to 10^{-1} torr at the high pressure. At low pressures the residence time in this cell is calculated to be $3 \times 10^{-3} \sqrt{M/T}$ sec, where M and T are the molecular weight and temperature.

The pyrolysis of toluene can be used as an example to illustrate the potential of the present approach for the study of high-temperature hydrocarbon chemistry. The mechanism for the high temperature pyrolysis of toluene at low pressures deduced from the present work may be summarized as follows:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + H \tag{1}$$

$$H + C_7H_8 \longrightarrow C_7H_7 + H_2 \tag{2}$$

$$H + C_7H_8 \longrightarrow C_6H_6 + CH_3 \tag{3}$$

$$C_7H_7 \longrightarrow C_5H_5 + C_2H_2 \tag{4}$$

$$C_7H_7 \longrightarrow C_4H_4 + C_3H_3 \tag{5}$$

$$C_5H_5 \longrightarrow C_5H_3 + H_2 \tag{6}$$

$$C_4H_4 \longrightarrow C_4H_2 + H_2 \tag{7}$$

$$C_4H_4 \longrightarrow C_4H_3 + H \tag{8}$$

At higher pressures we have also found evidence (from experiments using isotopically labelled compounds) suggesting the following reactions:

$$CH_3 + C_7H_7 \longrightarrow C_8H_8 + H_2 \tag{9}$$

$$CH_3 + C_6H_5CH_3 \longrightarrow C_6H_6 + C_2H_2 + (3H) \tag{10}$$
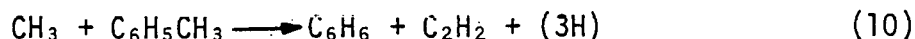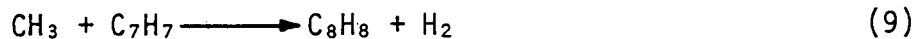
where (3H) refers to 3H or $H_2 + H$.

Reaction 1 is the only unimolecular reaction of toluene observed in this work. An alternate decomposition pathway suggested by a number of

workers at one time or another is unimportant in our experiments at temperatures below 1400°C.

$$C_6H_5CH_3 \longrightarrow C_6H_5 + CH_3 \qquad\qquad (11)$$
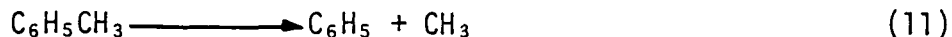
The concentration of C_6H_5 at low pressures indicates that the rate of reaction 1 is at least 200 times greater than reaction 11, in spite of the similar activation energies predicted for these reactions.

These and similar experiments are providing the first reliable <u>direct</u> analysis of the products of hydrocarbon pyrolysis <u>at high temperatures.</u> It should be noted that the large majority of previous work was carried out under quite different conditions, at higher pressures and lower temperatures than described in this work, and some differences are to be expected. While quite different mechanisms may function at higher temperatures, this is probably unusual since we have yet to find clear evidence of this on the basis of comparison to previous studies. The few previous mass spectrometric studies of such systems[11][12], have suffered from the absence of beam modulation techniques in addition to numerous other difficulties.

The bulk of previous work on hydrocarbon pyrolyses using conventional flow reaction techniques roughly corresponds to our studies at higher pressures. The product distributions observed at higher pressures are somewhat different from previous results due to the direct mass spectrometric sampling technique. In the present study, radicals and unstable molecular species are detected with nearly equal ease. For example, in early work on the pyrolysis of toluene Szwarc reported bibenzyl ($C_{14}H_{14}$) as the only higher molecular weight product.[13] Later workers have reported additional products, most of which correspond to stable species observed in our studies for toluene. The compounds which appear to have no corresponding product in our study (ethyl benzene, methyl biphenyl, stilbene, benzyl toluene, dimethyl diphenyl, and methychrysene) are most likely manifestations of the much higher pressures used in previous studies. The higher pressures allow rapid stabilization of reaction products in third order processes which might otherwise dissociate or eliminate one or two hydrogen molecules at low pressures used in the present work. The radicals observed in the present work would react further, ultimately producing stable molecules and perhaps contributing to the collection of unanalyzed high molecular weight products (tar) frequently reported in conventional flow reaction studies.

The concentration profiles as a function of temperature (e.g., see Figure 4) provide considerable insight into the nature of hydrocarbon stabilities at high temperatures. For toluene, the maximum concentration for all products of higher molecular weight than toluene are observed between 1300°C and 1400°C. Apparently, at temperatures higher than 1400°C, most larger species, or the radicals necessary for their formation, are increasingly unstable. At temperatures above 1700°C, no species heavier than C_6H_6 are observed at any pressure.

At the higher temperatures, another interesting phenomenon becomes evident. Above 1500°C and at higher pressures, we find that the products become dominated by species containing even numbers of carbon atoms (C_2 to C_{12}). Even the CH_3 concentration decreases, apparently due to reaction with other species containing odd numbers of carbon atoms. It should be noted that reaction of two CH_3 molecules is sufficiently exothermic that the products $C_2H_2 + 2H_2$ are thermodynamically allowed.

Most mechanisms postulated for the formation of soot in combustion processes involve either hydrocarbon radicals, polyacetylenes ($C_{2x}H_2$), or polycyclic aromatic hydrocarbons. The present results are of interest in this regard: each of these are formed readily and rapidly in the pyrolysis of the simple aromatic hydrocarbons examined. As shown in the figures, a number of reactive radicals are formed in the high temperature pyrolysis of toluene. In addition to the stable hydrocarbon products observed in this work (and observed previously by other workers), we have also observed polyacetylenes. Polyacetylenes are major species in acetylene and benzene flames[1-4], are formed in lesser amounts in the thermal decomposition of acetylene[8], and have been postulated to be important species in carbon formation in flames.[1-4]

While we have observed polyacetylenes up to C_8H_2, these species are present in relatively low abundances, and if reactive, form species other than higher polyacetylenes. The maximum concentrations of polyacetylenes in this work were observed at 1350°C. At higher pressures, the C_6H_2 and C_4H_2 concentrations continued to increase (possibly due to contributions from pyrolysis of C_6H_4 and C_4H_4), while C_8H_2 decreased, suggesting this species is quite reactive.

The formation of polycyclic aromatic hydrocarbons (PAH's) and their corresponding radicals (in many cases) occurs readily, requiring only a few gas-gas collisions. The possible role of these species in carbon formation during combustion has been postulated by many workers. The PAH's are of interest in themselves since most are known to be combustion products and many are mutagenic. The fact that species are readily formed under low pressures and are stable at high temperatures is consistent with the fact that they are known combustion products for nearly all fuel rich or turbulent systems.

Very little is known about the structure and reactivity of many of the radicals observed at higher temperatures. The simpler radicals, CH_3, C_3H_3, and C_4H_3, are observed in C_2H_2 combustion.[1-4] Other species observed in acetylene flames, such as C_2H and CH_2, were not detected in this work. The structures of other radicals such as C_5H_3 and C_7H_5 are certainly open to question. For heavier radicals (such as C_8H_7, C_9H_7, $C_{11}H_7$, $C_{11}H_9$, $C_{12}H_9$, etc.) many isomeric structures can be postulated and probably exist for these high temperature processes.

These experiments are presently being extended to include a wider range of aromatic compounds and to examine the species condensing and polymerizing on cool surfaces outside the reaction cell.

REFERENCES

[1] K. H. Homann, M. Mochizuki, and H. GG. Wagner, <u>Z. Physik. Chem. N.F.</u>, <u>37</u>, 299-313 (1963).

[2] K. H. Homann and H. GG. Wagner, <u>Ber. Bunsengesellschaft</u>, <u>69</u>, 20-35 (1965).

[3] U. Bonne, K. H. Homann, and H. GG. Wagner, Tenth Symposium (International) on Combustion, 503-512 (1965).

[4] K. H. Homann and H. GG. Wagner, Eleventh Symposium (Internation) on Combustion, 371-378 (1967).

[5] C. F. Cullis, I. A. Read, and D. L. Trimm, Eleventh Symposium (International) on Combustion, 391-397 (1967).

[6] S. C. Graham, J. B. Homer, and J. L. Rosenfeld, <u>J., Proc. Royal Soc. (London) A 344</u>, 259-285 (1975).

[7] W. C. Gardiner, J. H. Owen, T. C. Clark, J. E. Dove, S. H. Bauer, J. A. Miller, and W. J. McLean, Fifteenth Symposium (International) on Combustion, 857-868 (1975).

[8] I. D. Gay, G. B. Kistiakowsky, J. V. Michael, and H. Niki, <u>J. Chem. Phys.</u>, <u>43</u>, 1750-1726 (1965).

[9] R. D. Smith, <u>J. Phys. Chem.</u>, <u>83</u>, 1553 (1979).

[10] D. M. Golden, G. N. Spokes, and S. W. Benson, <u>Angew. Chem. Internat. Edit.</u>, <u>12</u>, 534 (1973).

[11] K. U. Ingold and F. P. Lossing, <u>Can. J. Chem.</u>, <u>31</u>, 30 (1953).

[12] G. N. Spokes and S. W. Benson, in: Recent Developments in Mass Spectrometry (K. Ogata and T. Hayakawa, Ed.), Baltimore, University Park Press, 1146 (1970).

[13] M. Szwarc, <u>J. Chem. Phys.</u>, <u>16</u>, 128 (1948).

FIGURE CAPTIONS

Fig. 1   Schematic illustration of the high-temperature Knudsen cell-modulated molecular beam mass spectrometer constructed for these studies. For precise alignment, the entire furnace assembly may be moved about the plane perpendicular to the molecular beam.

Fig. 2   Normalized phase-sensitive signal intensities (total signal = 100%) for the major species in the pyrolysis of benzene for 15 eV electron impact ionization and 10^{-3} torr pressure (at 1200°C) in a tungsten Knudsen cell having a 3 mm orifice.

Fig. 3   Apparent appearance potentials measured using the linear extrapolation technique for m/z 91 and m/z 92 in toluene as a function of temperature.

Fig. 4   Concentration as a function of temperature for the major products of toluene pyrolysis at a pressure of approximately 10^{-2} torr.

Fig. 5   Concentrations of C_7H_8, C_7H_7, C_2H_2, and CH_3 in a quartz Knudsen cell at 1280°C, as a function of pressure.

Fig. 6   Concentrations of C_7H_6, C_7H_5, C_6H_6, C_5H_5, C_4H_2, C_3H_3, C_2H_4, and CH_3 in a quartz Knudsen cell at 1280°C, as a function of pressure.