

KINETICS AND MECHANISMS FOR THE FORMATION OF ORGANIC
POLLUTANTS DURING PYROLYSIS AND COMBUSTION

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The potential toxicity and mutagenicity of emissions from coal fired plants are of continuing concern. Of these emissions, the organic aromatic pollutants probably represent the major mutagenic constituents. Aromatic compounds, soot and related compounds are known to be produced efficiently under many combustion conditions but their formation mechanisms have not been clearly established. In the last year, the Reaction Kinetics of Combustion Products Program has evolved from studies of flyash formation of aromatic pollutants.

A fundamental understanding of the kinetics and mechanisms for formation of aromatic pollutants is necessary for a number of reasons. An understanding of the high temperature chemistry can facilitate the development of effective control strategies based upon manipulation of combustion parameters. Similarly, information supplied from these fundamental studies provide necessary thermochemical data for equilibrium calculations or kinetic data for modelling studies. Other practical problems related to soot formation, heat transfer and combustion efficiency will also benefit from these data.

Studies of the polycyclic organic emissions from flames and various combustion facilities have shown that the emissions are qualitatively similar. Most aromatic compounds (or their precursors) ultimately emitted from coal combustion will result from the highly fuel rich local conditions of coal pyrolysis during the initial stages of combustion. An initial working assumption is that after formation the rates of the various oxidation and destruction pathways govern the emission concentrations. Thus, our initial approach has involved the study of simple aromatic model compounds (e.g., benzene, toluene, ethyl benzene, phenylacetylene, etc.) which may be formed during coal devolatilization. Our goal is to determine representative

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primary unimolecular and bimolecular rate data and to identify important reaction pathways for the formation and destruction of representative species. Measurements of rate constants as a function of temperature can be used to derive valuable thermochemical information and input for modelling calculations while mechanistic data provide a perhaps even more useful qualitative understanding of pollutant formation.

Part of the experimental equipment used in these studies has been described previously.^(1,2) Modulated molecular beam mass spectrometry, and related techniques such as phase angle spectroscopy, is used to analyze the products from high temperature reaction cells or flow tubes. The major advantage of this approach is the near universal nature of the detector; nearly equal sensitivities are obtained for both radicals and stable molecules. To obtain reliable quantitative or qualitative data from these studies, one must correct for, or avoid, thermal effects (e.g., the dependences of the mass spectral fragmentation pattern upon temperature and more subtle effects related to changes in molecular velocity). Our initial studies have examined the pyrolysis of a number of model compounds as a function of pressure and temperature. Mechanistic studies involving a number of additives (O_2 , N_2 , NO , SO_2) have also been carried out. Rate constants for the initial unimolecular pyrolysis processes have been determined as a function of temperature at low pressures; similar experiments are planned at elevated pressures. Initial heterogeneous studies involving surface reactions and condensation processes are being used to identify important high temperature intermediate species (e.g., CH_3 , C_2H_2 , C_3H_3 , C_4H_2 , C_5H_3 , etc.) in the formation of specific aromatic species obtained by quenching the molecular beam on surfaces at controlled temperatures and analyzed by GC-MS. Experiments with more complex heteroatomic species are also planned to study the chemistry of systems incorporating S, N, or O atoms.

Our results indicate the formation of higher molecular weight products has a maximum, as a function of temperature, in the 1200°C to 1400°C range for all aromatic systems studied thus far. This maximum is apparently nearly independent of pressure below about 10 torr. Initial results of the gas phase pyrolysis have supported the suggestion of two distinct routes for the formation of polycyclic aromatic hydrocarbons and soot. Below approximately 1450°C direct condensation of aromatic precursor, leads to higher molecular weight compounds, and ultimately some soot formation. At

higher temperatures initial pyrolysis reactions result in the formation of reactive lower molecular fragments (CH_3 , C_2H_2 , C_3H_3 , C_4H_2 , etc.), which are highly efficient in forming soot by heterogeneous processes but are less efficient in forming aromatic species (however, reaction does apparently speed greatly upon cooling). Our gas phase studies have also identified a number of highly reactive intermediate hydrocarbons for the formation of higher molecular weight compounds (e.g., C_3H_3 , C_4H_3 , C_5H_3 , and C_7H_7). Experiments are being planned to better define the heterogeneous chemistry of these high temperature aromatic systems, relate experimental results to actual combustion experiments and to explore equilibrium calculations for estimating the concentrations of important species at high temperatures.

References

1. R. D. Smith, J. Phys. Chem., 83, 1553 (1979).
2. R. D. Smith, Combust. Flame, 35, 179 (1979).