



Project Summary

Fuel Decomposition and Flame Reactions in Conversion of Fuel Nitrogen to NO_x

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An experimental and analytical research program was conducted to provide information on the chemical phenomena involved in the conversion of air and fuel nitrogen to NO_x . The program was divided into three tasks.

Under Task 1, Fuel Decomposition, the early (pre-flame) reactions of fuel nitrogen species were investigated using both one- and two-stage reactors. Additional inert pyrolysis experiments were carried out with several fuel oils. The oxidative pyrolysis experiments involved model compounds (pyridine, benzonitrile, NH_3 , and HCN), fuel oils, and coals. The Task 2 study (Combustion Kinetics) was carried out in a low-pressure flat-flame burner. The formation of "thermal," "prompt," and "fuel" NO was investigated in $\text{CH}_4\text{-O}_2\text{-N}_2$ flames doped with small amounts of NH_3 or HCN . In addition, the formulation of fuel NO was investigated in a $\text{H}_2\text{-CO-O}_2\text{-Ar-NH}_3$ flame. This simulated the combustion of future low-Btu fuel containing some NH_3 as an impurity. Calculations were made under Task 3, Data Analysis, on the $\text{H}_2\text{-CO-O}_2\text{-Ar-NH}_3$ flame using a detailed kinetic-diffusion model.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key

findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

An experimental and analytical research program was conducted to provide additional information on the chemical phenomena involved in the conversion of air and fuel nitrogen to NO_x in the combustion of fossil fuels. The experimental techniques developed under the previous program (EPA Contract 68-02-0635) were improved to permit the chemistry to be studied in more detail.

The program was divided into three tasks. The pyrolysis and oxidative pyrolysis of fuels and model fuel nitrogen compounds was investigated in quartz microreactors in Task 1. Low-pressure flat-flame burner studies were conducted under Task 2, and in Task 3 an attempt was made to fit some of the burner results to a preliminary kinetic-diffusion model. The flat-flame burner study was extended to investigate the formation of thermal (prompt) NO and fuel NO from a methane flame and the formation of fuel NO in a simulated low-Btu fuel (CO and H_2) flame.

Task 1 - Fuel Decomposition

Additional inert pyrolysis experiments were conducted under this task but the major effort involved oxidative pyrolysis.

Inert Pyrolysis

HCN yields were measured from coals, fuel oils, and alternative fuels under inert conditions. Most of the inert pyrolysis experiments were carried out in a two-temperature-zone reactor and it was established that most of the HCN is not produced directly in the primary vaporization-pyrolysis process but forms later in the secondary reactions of volatile nitrogen species. The alternative liquid fuels derived from coal and oil shale produced strikingly larger percentage yields of HCN. When the model fuel nitrogen compounds benzonitrile and quinoline were added to oils, the fraction of the model compound converted to HCN was about the same as was obtained with the model compound alone.

Oxidative Pyrolysis and Oxidation

In the oxidative pyrolysis experiments, the products were measured as a function of temperature for two model compounds (pyridine and benzonitrile), three oils, and one coal. Two-stage reactors were employed in some of the oxidative studies to investigate again the role of secondary reactions.

The model compounds were decomposed at a high oxygen concentration (75 percent) over a range of temperatures. The product distributions were quite similar in general with large amounts of HCN, NH_3 , and CO forming around 700°C from both pyridine and benzonitrile. At temperatures above 750°C, the major oxidation products are CO_2 , N_2 , N_2O and, in the case of benzonitrile, NO. The formation of large yields of N_2O (up to 45 percent) was quite unexpected.

Two-stage oxidative pyrolysis experiments established that the N_2 and N_2O observed at the higher temperatures formed in the secondary reactions of the NH_3 , HCN, and volatile tars formed in the primary reaction process. The oxidation of NH_3 and HCN alone was also investigated and N_2O was found to form in large yields from HCN (up to 50 percent) and as a minor product from NH_3 (about 10 percent). The addition of NH_3 to HCN was found to stabilize the HCN with respect to oxidative decomposition.

In the two-stage oxidation of fuel oils, only small amounts of N_2O (on the order of 5 percent) formed, but the oxygen concentrations were lower than in the model compound experiments. Minor amounts of N_2O (~2 percent) even formed in the oxidative pyrolysis of coal. In general, the presence of oxygen only increased slightly the HCN yields from fuel oil over those obtained under inert conditions. It was found that about 10 percent of the volatile nitrogen from a No. 6 fuel oil is in an extremely reactive form that, in the presence of some oxygen, can be converted to HCN at temperatures as low as 460°C. Only moderate amounts of NO formed in the oxidative pyrolysis of fuel oil.

Task 2 - Combustion Kinetics

Low-pressure flat-flame burner studies were conducted to investigate further the mechanisms and kinetics involved in the conversion of fuel-nitrogen intermediates (such as NH_3 and HCN) to NO_x in methane flames. In addition, the rates and mechanisms for the formation of thermal and fuel NO in the flame front were compared directly, and the formation of fuel NO from NH_3 (which could be present as an impurity) was investigated in a simulated low-Btu fuel ($\text{CO} + \text{H}_2$).

An experimental technique was developed in which NH_3 and HCN could be measured accurately at low concentrations in these 0.1 atm flames by oxidizing the NH_3 and HCN to NO and measuring the NO in a chemiluminescent analyzer. By employing a quartz probe and various combinations of selective catalytic converters and a chemical trap for HCN, each nitrogen species could be measured at various distances above the burner. Coated Pt/Pt-Rh thermocouples, used to obtain temperature profiles in the methane flames, were found to be unsatisfactory in the $\text{CO-H}_2\text{-O}_2\text{-Ar}$ flames.

The rates and mechanisms of formation of thermal (prompt) and fuel NO were compared by studying $\text{CH}_4\text{-O}_2\text{-N}_2$ and $\text{CH}_4\text{-O}_2\text{-Ar-NH}_3$ flames under identical conditions. Under fuel-rich conditions, both flames generated relatively high concentrations of HCN and both the prompt and fuel NO appeared to form through an HCN intermediate. The HCN profiles were very similar. Only about 25 percent as much prompt NO formed under fuel-lean conditions, indicating that prompt NO forms via the reaction of fuel fragments with N_2

resulting in the formation of the HCN intermediate (the Fenimore mechanism).

The $\text{CO-H}_2\text{-O}_2\text{-Ar-NH}_3$ flame, which was studied in detail only under fuel-rich conditions, gave some very unexpected results. The ammonia was converted to NO in high yield and then, just above the flame front, much of the NO was consumed and a small amount of the consumed NO reformed slowly far above the flame front. These results indicate that some very unusual nitrogen species form from NH_3 in this flame. It was shown that most of the NO consumption at the top of the luminous zone is promoted by nitrogen species. Very long-lived nitrogen species are also formed as evidenced by the slow formation of NO more than 40 mm above the burner and the observation that the added NH_3 changes the color of the flame even farther above the burner. When NO and NH_3 were added to the feed gas simultaneously, the rapid consumption of both the NO and NH_3 occurred below the luminous zone. Apparently a direct reaction occurs that is similar to that involved in the DeNO_x process.

Task 3 - Data Analysis

An attempt was made to fit the results obtained with the $\text{CO-H}_2\text{-O}_2\text{-Ar-NH}_3$ flame to a 59-reaction mechanism using a kinetic-diffusion model. The predicted concentration profiles for both the major species and the nitrogen species were quite different from those measured experimentally. This probably resulted both from the uncertainty in certain physical parameters, such as the temperature profile between the burner and the luminous zone, and from deficiencies in the reaction rate set. Interestingly, the kinetic model predicts that moderate concentrations of O_2 are present above the flame front of this fuel-rich flame and this was observed experimentally.

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The complete report, entitled "Fuel Decomposition and Flame Reactions in Conversion of Fuel Nitrogen to NO_x" (Order No. PB 82-108 358; Cost: \$21.50, subject to change) will be available only from:

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