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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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ABSTRACT

A study of the reaction mechanism which leads to NO formation from fuel-nitrogen by determining the rates and mechanisms of pyridine pyrolysis and cyanogen oxidation was continued. The emphasis was shifted to the determination of the rate of formation of HCN since in previous studies it was found to be the major product containing the nitrogen during pyridine pyrolysis at higher temperatures (essentially 100% of the nitrogen appeared as HCN at $1100^{o}C$). Because of the unreliability found in data from HCN chromatographic peak heights, the determinations are being done by wet chemical methods and these experiments are just underway. The oxidation of cyanogen has concentrated on a material balance. Using a one meter gas cell, infrared spectra of the products indicate that CO_2 is the only major oxidation product in the $950-1050^{o}C$ range. Small amounts of N_2O were found but no NO was observed; thus, it appears that most of the nitrogen from the reaction ends up in the elemental form. The significance of these observations to the overall project is that NO_x formation from fuel-nitrogen appears minor if fuel pyrolysis to CN type species takes place before oxidation. However, since fuel-nitrogen does contribute significantly to NO_x formation during coal combustion, the oxidizer must influence the products during the pyrolytic stage.

OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollution. The emission of NO and other oxides of nitrogen from various combustion devices is a serious contributor to that pollution. The source of NO during the combustion process may be atmospheric nitrogen or nitrogen-containing compounds in the fuel. In order to predict NO emission for the formulation of suitable analytical models, it is necessary to have accurate kinetic data and a reasonable reaction mechanism for the formation of NO.

The objective of this research program is to obtain kinetic and product distribution data from which a mechanism may be proposed for the formation of NO from fuel nitrogen. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) will be studied. In addition, similar oxidative studies will be made on representative, condensed-ring heterocycles, e.g. quinoline, carbazole, etc. to determine the extrapolatability of the results obtained with pyridine to more coal like structures. The oxidation of volatile, nitrogen-containing pyridine pyrolysis products, e.g. cyanogen, HCN, vinylcyanide, etc., will also be carried out to help elucidate the mechanism of NO formation.

The experimental approach will involve the use of a stirred-flow reactor to obtain differential rate data which will aid in interpretation of complex kinetic data. On stream mass spectrometric, gas chromatographic and infrared spectrophotometric monitoring of products and reactants will be carried out also.

SUMMARY OF PROGRESS

Task 2, which consists of experiments to determine the rate and mechanism of pyrolysis of pyridine in an inert atmosphere, has been about 90% completed. No adjustment has been made to this figure during the report period because, as with many research projects, additional information becomes necessary as the program proceeds, thus postponing completion. During this period, the emphasis was shifted to the determination of the rate of formation of HCN, since at higher temperatures in previous studies it was found to be the major product containing the nitrogen from pyrolized heterocycles (at 1100°C essentially 100% of the nitrogen appeared as HCN). The first technique tried, that of calibrating chromatographic peaks heights, proved unreliable. Therefore, a wet chemical, picric acid-colorometric, method was adopted. The initial results at 1000°C appear reasonable and these experiments are now underway. The techniques developed here will be useful in Task 3, the oxidative pyrolysis study.

Task 4, which is concerned with the oxidation of nitrogen-containing intermediate species was continued with the study of the oxidation of cyanogen. The work concentrated on the determination of a material balance, for which the MS-10 mass spectrometer proved to be essentially useless. Infrared spectra from a one meter gas cell gave the qualitative information that CO_2 was the only major oxidation product in the 950-1050°C range. Small amounts of N_2O were observed but no NO was found; thus, it appears that most of the nitrogen from the reaction ends up in the elemental form. The significance of these observations to the overall project is that NO_x formation from fuel-nitrogen appears minor if fuel pyrolysis to CN type species takes place before oxidation. However, since fuel-nitrogen does contribute significantly to NO_x formation during coal combustion, the oxidizer must influence the products during the pyrolytic stage to reduce CN formed. The objective of Task 3 is to determine this influence.

DETAILS OF TECHNICAL PROGRESS

Task 2

Work concentrated on a better definition of the mechanism of pyridine pyrolysis and HCN formation, after the repairs to the apparatus were completed as described in the previous report (1). The first attempt to determine the rate of production of HCN gave results which were clearly impossible, specifically the ratio of moles HCN produced to moles pyridine decomposed was significantly greater than one in a large fraction of the experiments. The faulty analytical technique employed the Liebig wet chemical method (2) to calibrate the HCN gas chromatograph peak then subsequently this peak was used to measure moles of HCN formed. Because of these misleading results, it was decided to make all the determinations by a wet chemical technique (in all probability it was the complexity of chromatogram rather than the titration that lead to the error) and to choose a method that would be more rapid than by titration.

The following Picric Acid-Colorometric approach (3) has been adopted for the HCN analyses:

(a) Calibration of Absorbance. A standard stock solution was prepared using KCN with an equivalent concentration of 1000 ppm HCN. This solution was further diluted to make up four solutions of 10, 20, 50 and 100 ppm HCN. To 5 ml aliquots of these solutions in 100 ml volumetric flasks was added 5 ml of 0.5 molar Na_2CO_3 followed by 5 ml of 1 wt % picric acid solution, immediately after which the flasks were immersed in a boiling water bath for 5.0 min. Time and volumes are critical for reproducible results. After removal from the bath, the solutions were quickly diluted to 100 ml to give the calibration concentrations reported in the table.

Calibration Data*

Absorbance	ppm HCN
0.057	0.50
0.115	1.00
0.334	2.50
0.646	5.00

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*Read at 520 nm with a 0.02 mm slit and 1 cm cells.

It should be noted that additions of a large excess of pyridine to the standard solutions did not change the absorbance significantly.

(b) Collection and Analysis of HCN. A bubbler containing 125 ml of 0.5 M Na_2CO_3 solution was attached for a measured period of time to the exhaust of the stirred-flow reactor after steady-state flow conditions had been reached. (A second bubbler in series with the first revealed that essentially no HCN was passing through the first.) The extent of reaction was checked gas chromatographically before and after the sample collection. The sample solution was diluted by a factor of 2, then a 10 ml aliquot of this was diluted to 100 ml with a 0.25 M Na_2CO_3 solution. A 10 ml aliquot of this solution is combined with 5 ml of 1% picric acid in a 100 ml volumetric flask and this mixture treated as in the calibration procedure. The absorbance of this solution is read on the spectrophotometer against a blank solution.

The above procedure is being applied to the decompositions over a range of conditions. To date the results of a few experiments at $1000^{\circ}C$

show a ratio of moles HCN/moles pyridine decomposed of about .5 with some deviations. These and the results from subsequent experiments will be discussed in the next report.

Task 4

Following the conclusion of the oxidation of cyanogen rate experiments in the 950 to 1050°C range, an attempt is being made to determine the products which are being formed during the reaction. The MS-10 was of no value for these investigations, nothing other than reactants was appearing down stream from the reactor in a significantly higher concentration than the background. This prompted the use of a 1 meter IR gas cell which indicated that CO_2 was the only major oxidation product; some N_2O was formed but under these conditions no NO was found. Thus, most of the nitrogen produced must be in the elemental state. These observations were only qualitative, but quite definitive.

The observation of N_2O rather than NO is surprising in two respects: (a) the free energies of formation do not favor either NO or N_2O, and in addition, N_2O was the more thermodynamically unstable (4) (a mixture of only N_2 and O_2 gave no NO_x under these conditions as was expected), and (b) it is difficult to construct a transition state or an intermediate that would lead to N_2O rather than NO.

Based on the limited data it appears that if pyrolysis of the fuel results in CN formation before the oxidizer can reach it, the formation of nitrogen oxides at lower temperatures is of minor importance and probably a Zeldovich type mechanism becomes a more important source of NO_x as temperatures are increased. However, since NO_x formation is strongly dependent on fuel nitrogen in coal burner operation (5), it appears likely that the oxidizer is influencing the product distribution in the pyrolytic zone prior to CN formation. The pursuit of this information will be the objective of Task 3.

Work is continuing on quantitative measurement of CO_2 formed during reaction.

Tasks 1, 3, 5 and 6

Task 1 will be completed with the assembly of the quadrupole mass spectrometer, which has been postponed because of the other experiments currently being carried out; the other tasks will be undertaken at a later date.

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