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Nitrogen Oxide Formation From Chemically-Bound Nitrogen During the Combustion of Fossil Fuels

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NITROGEN OXIDE FORMATION FROM CHEMICALLY-BOUND NITROGEN DURING THE COMBUSTION OF FOSSIL FUELS

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ABSTRACT

One of the many problems associated with the firing of fossil fuels for the generation of electricity and process steam is the impact on the ambient levels of nitrogen oxides. Since the use of coals, oils and coal-derived fuels is expected to triple by 1985, it is urgent that the formation of nitrogen oxides from molecular nitrogen and organo-nitrogen species be fully characterized so that emission abatement strategies can be formulated.

The thermal fixation of atmospheric nitrogen and the free radical reactions of nitrogenous species are the sources of NO_x during the combustion of fossil fuels. The fixation reactions can be described by the extended Zeldovich mechanism, and techniques such as staged combustion and flue gas recirculation have been employed to reduce combustion temperatures and, hence, thermally formed NO. These techniques have had little effect, however, on the conversion of chemically-bound nitrogen to NO_x. The fate of chemically-bound nitrogen depends upon such factors as the nitrogen content of the fuel and the equivalence ratio and upon the physical processes governing combustion.

Research is proposed to establish the kinetic processes involved in the conversion of fuel nitrogen to NO and N_2 in environments characteristic of fossil fuel combustion and to identify those conditions which favor the reduction of NO to N_2. It is hoped that, as a result of such knowledge, new approaches to emission control will become evident and the environmental problems associated with coal use resolved.

INTRODUCTION

One of the many problems associated with the firing of fossil fuels for the generation of electricity and process steam is the impact on the ambient levels of nitrogen oxides. The substantial quantities of nitrogen in oils, coals and coal-derived fuels would have little significance if it were not for the fact that nitrogen tends to be reactive, readily forming nitrogen oxides. Unfortunately, there is no known economic method of removing these oxides; the best solution appears to be to prevent their formation in the first place. Since the use of coal and coal-derived fuels in conventional and advanced combustion systems such as MHD generators, fluidized beds and direct-fired gas turbines is expected to triple by 1985, it is urgent that the formation of nitrogen oxides from molecular nitrogen and fuel nitrogen species be fully characterized so that emission abatement strategies can be formulated.

Nitrogen oxide formation during the combustion of fossil fuels is due to the thermal fixation of atmospheric nitrogen and to the radical reactions of chemically-bound nitrogen. The fixation reactions are described by the modified Zeldovich mechanism[1-5] and techniques such as staged combustion[6-8] and flue gas recirculation[7,8] have been employed to reduce combustion temperatures and, hence, thermally formed NO. These techniques have had little effect, however, on the conversion of chemically-bound nitrogen to NO_x.[9] Observations of NO_x formation from fuel nitrogen in flames and in coal and oil-fired combustors have led to the following conclusions:[9-15]

- The fractional conversion of chemically-bound nitrogen to NO_x decreases with an increase in the nitrogen content of the fuel and appears to be relatively independent of organo-nitrogen type.

- Increases in the fuel/air equivalence ratio decreases the rate of conversion of fuel nitrogen to NO_x.

- The conversion of fuel nitrogen to NO_x is not a strong function of temperature, but tends to increase with increasing temperature.

Currently, research is needed in order to obtain a better understanding of the important processes involved in the production of nitrogen oxides from chemically-bound nitrogen. The proposed research is aimed at determining the fate of chemically-bound nitrogen during the combustion of nitrogen-containing fuels. Key nitrogen intermediates will be identified and important reaction mechanisms and kinetic data will be established. This experimental and theoretical effort should lead to the determination of those factors which influence the formation of nitric oxide during the combustion of fossil fuels. It is hoped that as a result of such knowledge, new approaches to emission control may become evident and the environmental problems associated with coal use resolved.

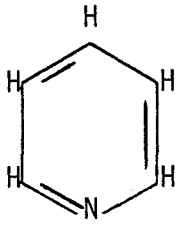
BACKGROUND INFORMATION

Coal and coal-derived fuels are composed primarily of condensed aromatic rings of high molecular weight. About 70% of the carbon atoms are in these rings and about 20% of the hydrogen atoms are attached to aromatic carbon atoms. Oxygen, sulfur and nitrogen are combined in chemically functional groups which occur as integral parts of the molecule. Although it is difficult to determine the exact structures of the nitrogen groups, it has been established that they are mainly heterocyclics. The most important classes of heterocyclic nitrogen compounds include pyridines, quinolines, pyrroles, indoles, carbazoles, phenazines and quinolones. These compounds are illustrated in Table I. Nitrogen also occurs in benzonitrite and aniline groups distributed throughout the molecule.

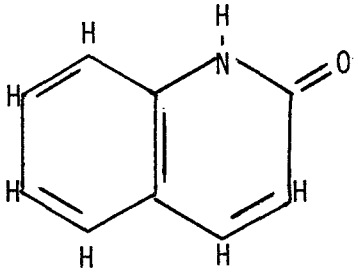
Table II shows that the nitrogen content of typical coals used for power generation ranges from about 1.0 to 2.0 percent. The last row of this table indicates that about four pounds of NO_x per million Btu could be expected if all the nitrogen in the coal were converted to nitrogen oxides. It has been experimentally observed, however, that in most combustion systems only a fraction of the chemically-bound nitrogen is converted to NO_x.[9-15] This fraction is typically greater than 0.2 and depends on such parameters as fuel/air equivalence ratio and fuel nitrogen content. The critical point is that even if thermally formed NO_x were completely eliminated, the EPA standard of 0.7 pound NO_x per million Btu can be exceeded.

TABLE I. HETEROCYCLIC NITROGEN COMPOUNDS*

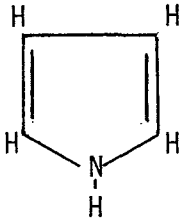
Pyridine



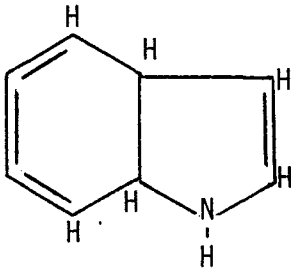
Quinolone



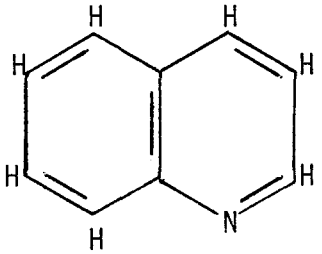
Pyrrole



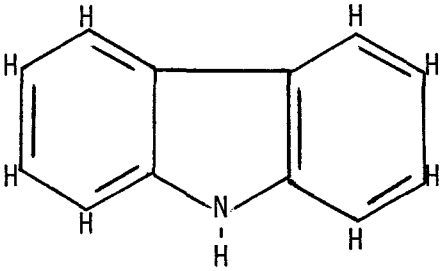
Indole



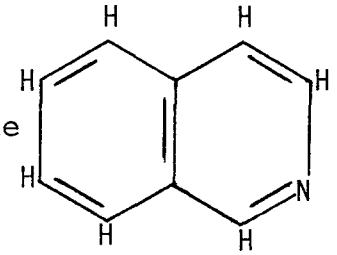
Quinoline



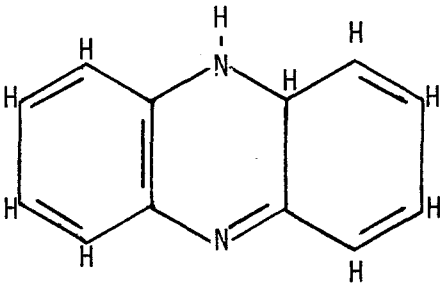
Carbazole



Iso-Quinoline



Phenazine



* Substituted homologs occur in fossil fuels.

TABLE II. COAL ANALYSIS (% BY WEIGHT, AS-RECEIVED BASIS)

State Mined:	Virginia	Kentucky	New Mexico	Pennsylvania	Montana
Coal Type:	Bituminous	Bituminous	Bituminous	Bituminous	Subbituminous
ASTM Rank	HVA	HVB	HVC	Low Volatile	B
Proximate Analysis					
% Moisture	0.97	6.11	11.07	1.01	19.84
% Ash	6.32	8.36	7.85	9.68	7.34
% Volatile	30.20	37.25	35.67	17.95	31.28
% Fixed Carbon	62.51	48.28	45.41	71.36	41.54
Heating Value, Btu/lb	14506.	12345.	11159.	13731.	9366.
Ultimate Analysis					
% Carbon	81.53	67.99	63.02	78.79	54.82
% Hydrogen	4.95	4.75	4.62	4.26	3.72
% Nitrogen	1.90	2.07	1.33	1.07	0.79
% Sulfur	0.56	1.51	0.63	0.55	0.34
% Oxygen (difference)					
lb $NO_2/10^6$ Btu*	4.31	5.52	3.92	2.56	2.77

* Calculated based on 100% conversion of fuel nitrogen to NO_x.

Amine and Organic Cyanide Reactions

In Tables III, IV and V, the reactions that may be important in the high-temperature combustion of amines and organic cyanides are listed. The amine reactions have received more consideration; in Table III rate constant expressions and the values of the rate constants at 1500° and 2000°K are given. With these values, judgments about competing reactions can be made at typical combustor and flame temperatures. Absolute comparisons cannot be made because the rates are proportional to the reactant concentrations which depend on combustion conditions.

The amine reactions are separated into three groups. The first and second groups consist of reactions of ammonia to form amidogen (NH_2) and amidogen to form imidogen (NH), respectively, while the third group consists of reactions of imidogen. The third group of reactions is especially interesting because feasible routes to NO and possible routes to N_2 are included. Also indicated is the formation of nitrogen atoms from imodogen. These atoms can react via the extended Zeldovich mechanism (Table V) which provides additional routes to NO and N_2 formation. The combustion of amines can be depicted graphically as follows:

$$\begin{array}{ccccccc} NH_3 & \rightleftarrows & NH_2 & \rightleftarrows & NH & \rightleftarrows & N \\ & & & & \swarrow \searrow & \swarrow & \searrow \\ & & & & NO & N_2 & NO \end{array}$$

Little is known about the reactions of organic cyanides at elevated temperatures. In Table IV, some reactions which need consideration when discussing the combustion of hydrogen cyanide are listed. Reliable rate data for these reactions do not exist; therefore, the heats of reaction are shown. The exothermic reactions have a higher driving force and, hence, a higher probability of occurrence.

The conversion of fuel nitrogen to nitrogen oxides depends upon the oxidant-temperature and time-temperature histories to which the nitrogen-containing species are subjected. Therefore, the distribution of nitrogen between the volatile matter and the char is important. Data on the distribution of nitrogen in coals and oils are limited, but Sternling and Wendt[15] analyzed fragmentary data and estimated that about 80% of the nitrogen in coals and about 60% of the nitrogen in oils appear in the char. The remainder of the nitrogen is in the volatiles and is released during devolatilization and vaporization as low molecular weight organic cyanides and amines.

The nitrogenous species formed during pyrolysis and oxidation of the fuel nitrogen react and result in NO and N_2 formation. Organic cyanides and amines are postulated to be the key intermediates. Potential paths of chemically-bound nitrogen during the combustion of fossil fuels are shown in the following diagram.

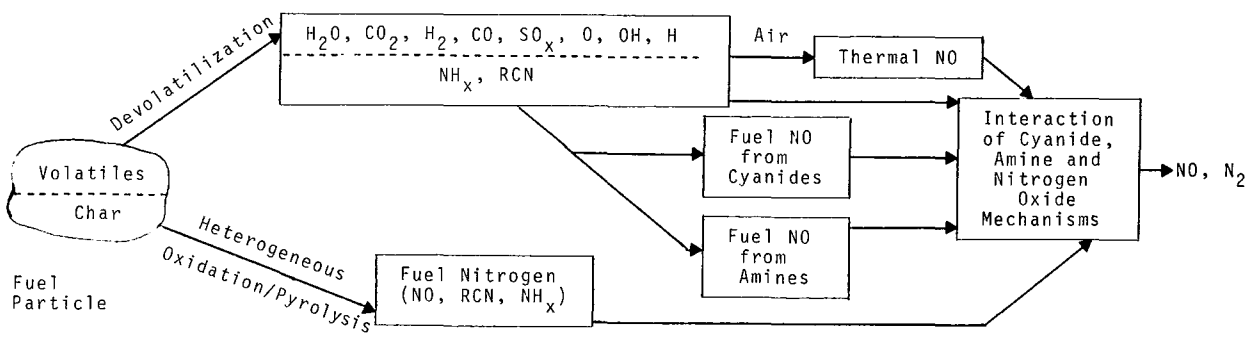


Figure 1. Potential Paths of Chemically-Bound Nitrogen During the Combustion of Fossil Fuels

A discussion of the reactions of amines and organic cyanides that may be important during the combustion of coals, oils and coal-derived fuels follows.

TABLE III. REACTIONS INVOLVING AMINES

Reaction	Forward Rate Constant Expression* a	b	c	k(1500°K)	k(2000°K)
1. $NH_3 + H = NH_2 + H_2$	$1.9 * 10^{11}$	0.67	3400.	$8.15 * 10^{12}$	$1.31 * 10^{13}$
2. $NH_3 + O = NH_2 + OH$	$8.2 * 10^{11}$	0.50	0	$3.18 * 10^{13}$	$3.67 * 10^{13}$
3. $NH_3 + OH = NH_2 + H_2O$	$4.0 * 10^{10}$	0.68	1100.	$4.00 * 10^{12}$	$5.33 * 10^{12}$
4. $NH_3 + N = NH_2 + NH$	$2.1 * 10^{11}$	0.50	23,160	$3.43 * 10^{9}$	$2.77 * 10^{10}$
5. $NH_2 + H = NH + H_2$	$1.4 * 10^{11}$	0.67	4300.	$4.44 * 10^{12}$	$7.72 * 10^{12}$
6. $NH_2 + O = NH + OH$	$9.2 * 10^{11}$	0.50	0	$3.56 * 10^{13}$	$4.11 * 10^{13}$
7. $NH_2 + OH = NH + H_2O$	$3.0 * 10^{10}$	0.68	1300.	$2.80 * 10^{12}$	$3.80 * 10^{12}$
8. $NH_2 + NH_2 = NH_3 + NH$	$1.7 * 10^{11}$	0.63	3600.	$5.09 * 10^{12}$	$8.25 * 10^{12}$
9. $NH_2 + NO = N_2 + H_2O$	$1.2 * 10^{10}$			$1.20 * 10^{10}$	$1.20 * 10^{10}$
10. $NH + H = N + H_2$	$1.0 * 10^{12}$	0.68	1900.	$7.64 * 10^{13}$	$1.09 * 10^{14}$
11. $NH + O = N + OH$	$8.4 * 10^{12}$	0.70	100.	$1.30 * 10^{15}$	$1.67 * 10^{15}$
12. $NH + O = NO + H$	$5.0 * 10^{11}$	0.50	5000.	$3.62 * 10^{12}$	$6.35 * 10^{12}$
13. $NH + OH = N + H_2O$	$1.6 * 10^{12}$	0.56	1500.	$5.81 * 10^{13}$	$7.74 * 10^{13}$
14. $NH + OH = NO + H_2$	$1.6 * 10^{12}$	0.56	1500.	$5.81 * 10^{13}$	$7.74 * 10^{13}$
15. $NH + N = N_2 + H$	Unavailable			--	--
16. $NH + H_2 = NH_2 + H$	$1.0 * 10^{11}$	0.49	21,470	$1.07 * 10^{10}$	$7.47 * 10^{10}$
17. $NH + O_2 = NO + OH$	Unavailable			--	--
18. $NH + NH = N_2 + H_2$	$3.6 * 10^{11}$	0.55	1900.	$1.06 * 10^{13}$	$1.46 * 10^{13}$
19. $NH + NO = N_2 + OH$	$2.4 * 10^{12}$			$2.4 * 10^{12}$	$2.4 * 10^{12}$

* $k = aT^b \exp(-c/RT)$ cm^3/mole-sec
Rate expressions obtained from the compilation of Reference 16 except for reactions 9 and 19 which were obtained from Reference 17.

TABLE IV. REACTIONS INVOLVING ORGANIC CYANIDES*

Reaction	Heat of Reaction (kcal/mole)
20. $HCN + H = CN + H_2$	19.6
21. $HCN + O = CN + OH$	21.6
22. $HCN + O = NCO + H$	-23.8
23. $HCN + OH = CN + H_2O$	4.47
24. $HCN + O_2 = NCO + OH$	-6.87
25. $CN + O = N + CO$	-77.0
26. $CN + O_2 = NO + CO$	-108.8
27. $CN + O_2 = NCO + O$	-28.4
28. $CN + NO = CO + N_2$	-152.0
29. $CN + CN = C_2 + N_2$	-7.78
30. $CN + NH = CH + N_2$	-43.0
31. $NCO + O = NO + CO$	-80.4
32. $NCO + O_2 = NO + CO + O$	38.7
33. $NCO + NCO = CO + CO + N_2$	-84.8
34. $NCO + N = N_2 + CO$	-155.4

*Heat of formation data from JANAF Thermochemical Tables except for that of NCO (16 kcal/mole) taken from Setser and Thrush, Proc. Roy Soc., A288, 1965, p. 275.

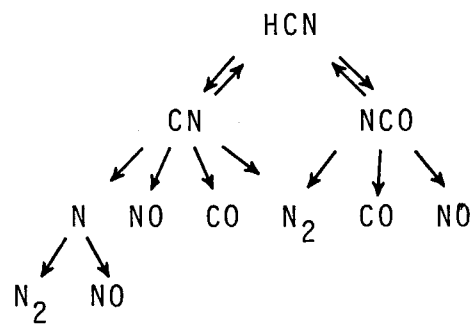
TABLE V. EXTENDED ZELDOVICH REACTIONS

	Reaction	Rate Constant Expression*			k(1500°K)	k(2000°K)
		a	b	c		
34a.	$N_2 + O \rightarrow NO + N$	$1.36 * 10^{14}$	0	75,400	$1.40 * 10^{3}$	$7.83 * 10^{5}$
34b.	$NO + N \rightarrow N_2 + O$	$1.62 * 10^{13}$	0	260.**	$1.48 * 10^{13}$	$1.52 * 10^{13}$
35a.	$N + O_2 \rightarrow NO + O$	$1.05 * 10^{10}$	1.0	6510.**	$1.78 * 10^{12}$	$4.10 * 10^{12}$
35b.	$NO + O \rightarrow N + O_2$	$2.36 * 10^{9}$	1.0	38,600	$8.40 * 10^{6}$	$2.85 * 10^{8}$
36a.	$N + OH \rightarrow NO + H$	$8.06 * 10^{13}$	0	2550.**	$3.42 * 10^{13}$	$4.24 * 10^{13}$
36b.	$NO + H \rightarrow N + OH$	$2.22 * 10^{14}$	0	50,500	$9.73 * 10^{6}$	$6.72 * 10^{8}$

* $k = aT^b \exp(-c/RT)$ cm^3/mole-sec
Rate constant expression for reaction 34 obtained from Reference 18.
Rate constant expressions for reactions 35 and 36 obtained from Reference 19.

** Determined from reverse rate constant and equilibrium constant.

The reactions listed show that hydrogen cyanide can be attacked by H, O and OH radicals and molecular oxygen to form cyano (CN) and fulminate (NCO) radicals. These radicals can be oxidized to form CO and NO, or can be combined with other nitrogenous species to form N_2. Schematically, cyanide combustion can be represented as follows:



Tables III, IV and V indicate the competitive paths of NO and N_2 formation from ammonia and hydrogen cyanide. The fractional conversion of NH_3 and HCN to NO depends upon such local factors as the oxygen concentration and temperature. During the combustion of fossil fuels, in fuel-rich regions of the combustor, nitrogen compounds must actively compete with hydrocarbon pyrolysis products for oxygen, and N_2 formation is favored. When oxygen is abundant, the conversion of nitrogen species to NO is expected. However, as N_2 and NO diffuse throughout the combustion system, they are subject to further reaction. Therefore, the NO_x emissions from fossil fuel-fired systems are critical functions of the temperature-time and concentration-time histories that the nitrogenous species experience.

NO and N_2 Formation During Fossil Fuel Combustion

The fate of chemically-bound nitrogen during the combustion of fossil fuels depends upon the physical processes governing combustion. Because of the low volatility of coals, oils and coal-derived fuels, premixing with combustion air to form a gaseous mixture is ineffective; therefore, fossil fuel-fired systems usually operate as diffusion flames. In diffusion flame combustion of particles, the particle size and heating rate, and the relative velocities between the particle and the surrounding gas are the most important parameters which influence the burning characteristics. For very high devolatilization rates and large relative velocities between the particle and the surrounding gas, combustion occurs in the wakes trailing the particle and the gaseous fuel and oxidizer are premixed before combustion starts. The burning is then accomplished largely under fuel-lean conditions. In these regions of high O, OH and O_2 concentrations, a suitable mechanism of amine combustion would consist of reactions 2, 3, 6, 7, 11, 13, 14 and 17; and the conversion of amine functional groups to NO appears to be favored. Similarly, cyanide conversion to NO appears favorable in these regions through such exothermic reactions as 22, 24, 25, 26, 27 and 31. These same reactions could be dominant in the trailing wakes of droplets when vaporization rates are high.

The kinetics of devolatilization is such that as the heating rate increases, a particle can attain an increasingly high temperature prior to the onset of significant devolatilization. At particle heating rates of the order 10^5 °C/sec, calculations[20] based on devolatilization data indicate that the temperature of small particles can exceed the ignition temperature for heterogeneous combustion of the solid before devolatilization becomes fast enough to support gaseous combustion away from the particle surface. A flame, therefore, attaches itself to the particle and most of the combustion occurs in a thin flame sheet surrounding

the particle and its wake. It has been suggested[20] that even large particles burn in this manner because they do not produce a great enough flux of volatiles to support a gaseous diffusion flame away from the surface. The smaller surface area-to-volume ratio of a larger particle is offset by its slower rate of temperature rise, which leads to simultaneous devolatilization and heterogeneous combustion at the particle surface.

Within the reaction zone surrounding the particle and its wake, fuel-rich conditions exist and pyrolysis occurs due to the low oxygen concentration. Equilibrium calculations show that if solid carbon is formed, ammonia can be converted to hydrogen cyanide. The study by Axworthy[21] on the pyrolysis of pyridine, quinoline, benzonitrite and pyrrole suggests that hydrogen cyanide is a key fuel nitrogen intermediate. Therefore, the reactions listed in Table IV are important in the reaction zone; and due to the low oxygen level, N_2 formation is expected to be favored. The observations of Sarofim, et al.[14] and Mitchell[22] support the formation of N_2 in the fuel-rich regions. They report 80-90% reduction of NO in the fuel-rich regions of hydrocarbon diffusion flames. These investigators hypothesize that hydrocarbon pyrolysis products can react with NO to form organic cyanides and amines via such reactions as

$$CH_x + NO \rightarrow NH_x + CO$$

$$CH_x + NO \rightarrow OH_x + CN \qquad x = 1, 2$$

which combine to form N_2. Kinetic calculations by Sternling and Wendt[15] indicate that the Zeldovich mechanism may also be important in NO reduction to N_2 in the fuel-rich regions of combustion systems.

For both large and small particles, as the devolatilization rate decreases due to a decrease in volatile matter, the flame front approaches the particle surface until oxygen molecules can attack the char directly. At the particle surface, carbon is converted to CO and nitrogen to nitric oxide or an organic cyanide which is readily oxidized to NO. However, as the NO diffuses away from the surface, it can be reduced by reburning in the CO diffusion flame surrounding the particle.

It is evident that before the conversion of fuel nitrogen to N_2 and NO can be fully characterized, the competitive reactions of key nitrogenous intermediates must be quantitatively evaluated. The remainder of this report outlines a research program designed to obtain the needed kinetic data and to identify the mechanisms by which chemically-bound nitrogen is converted to nitrogen oxides in environments characteristic of those found during the combustion of fossil fuels.

STATEMENT OF WORK

The proposed research is aimed at identifying the paths of fuel nitrogen conversion to molecular nitrogen and nitric oxide during the combustion of nitrogen-containing fuels. An extensive experimental and theoretical investigation will be initiated to determine the mechanisms of ammonia and hydrogen cyanide combustion at elevated temperatures and to identify key intermediates during the combustion of more complex nitrogen-containing compounds. Also, the interaction of nitric oxide with other combustion products will be investigated so that conditions which favor NO reduction can be identified. Each of these research areas are discussed in more detail below.

A systematic study of the combustion of hydrogen cyanide and of ammonia will be undertaken. Shock tube studies will be employed to determine pyrolysis and oxidation mechanisms. Infrared emission from nitric oxide and the amine species and the violet emission from the $CN(B^2\Sigma^+) \rightarrow CN(X^2\Sigma^+)$ band will be used as diagnostics. The rates of elementary steps will be inferred from comparisons of the measured HCN, NH_3 and NO histories and those histories predicted by a suitable model of the chemically reacting system. Values of critical rate constants will be determined theoretically and compared with the experimental results. Rate constant expressions determined will be used in a theoretical model designed to predict the distributions of nitrogen-containing species in flames. The model will be validated by comparison of the predicted NO and N_2 profiles with those experimentally determined by probing hydrocarbon/oxygen/argon diffusion flames doped with model nitrogen compounds. Spectroscopic and microprobe

techniques will be employed as diagnostic tools. Ammonia, hydrogen cyanide, methylamine and pyridine will be used as the model compounds. Emphasis will be placed on identifying the dominant intermediates and determining those flame conditions which tend to favor the conversion of fuel nitrogen to molecular nitrogen.

Obviously, the model developed will have to allow for full interaction between fluid dynamics and chemistry. Work has already begun on the development of a model of axisymmetric, chemically reacting, recirculating flows where allowance is made for variable thermodynamic and transport properties and reaction kinetics of the major combustion species. After validation, the model can be theoretically doped with nitrogenous species; and the fate of the chemically-bound nitrogen can be analytically determined and, hence, hypothesized mechanisms tested.

Having determined the combustion mechanisms of ammonia and hydrogen cyanide, more complex nitrogen compounds typical of those found in fossil fuels can be investigated. Pyridines, pyrroles, indoles, carbazoles and phenazines will be sample gases in shock tubes and an attempt will be made to identify key intermediates during their pyrolysis and oxidation. Although HCN has been identified as the major nitrogen-containing product of inert-pyrolysis of these compounds, the key intermediates during oxidative-pyrolysis have yet to be determined. Determination of these intermediates is essential if the fate of nitrogen bound in coals, oils and coal-derived fuels in fuel-rich environments is to be determined.

The combustion conditions which favor the reduction of nitric oxide to molecular nitrogen will be determined by studying NH_3/NO/inert, HCN/NO/inert and CO/NO/inert mixtures. By analyzing shock-heated samples of these mixtures, needed rate data can be obtained and important intermediates identified. The resultant rate constant expressions will be used in a model of a flow

reactor. In this model, the concentration-time histories of nitric oxide, ammonia and hydrogen cyanide can be followed as combustion gases doped with amine-reducing agents flow through the system. Various investigators[23,24] have observed that amine compounds are effective in decreasing the NO_x content of combustion gases. This model will help determine whether NO_x is being converted primarily to N_2 or if significant quantities of HCN and NH_3 are produced as well. Those conditions which favor the reduction of NO_x to N_2 will be determined, and the effectiveness of various reducing agents will be examined.

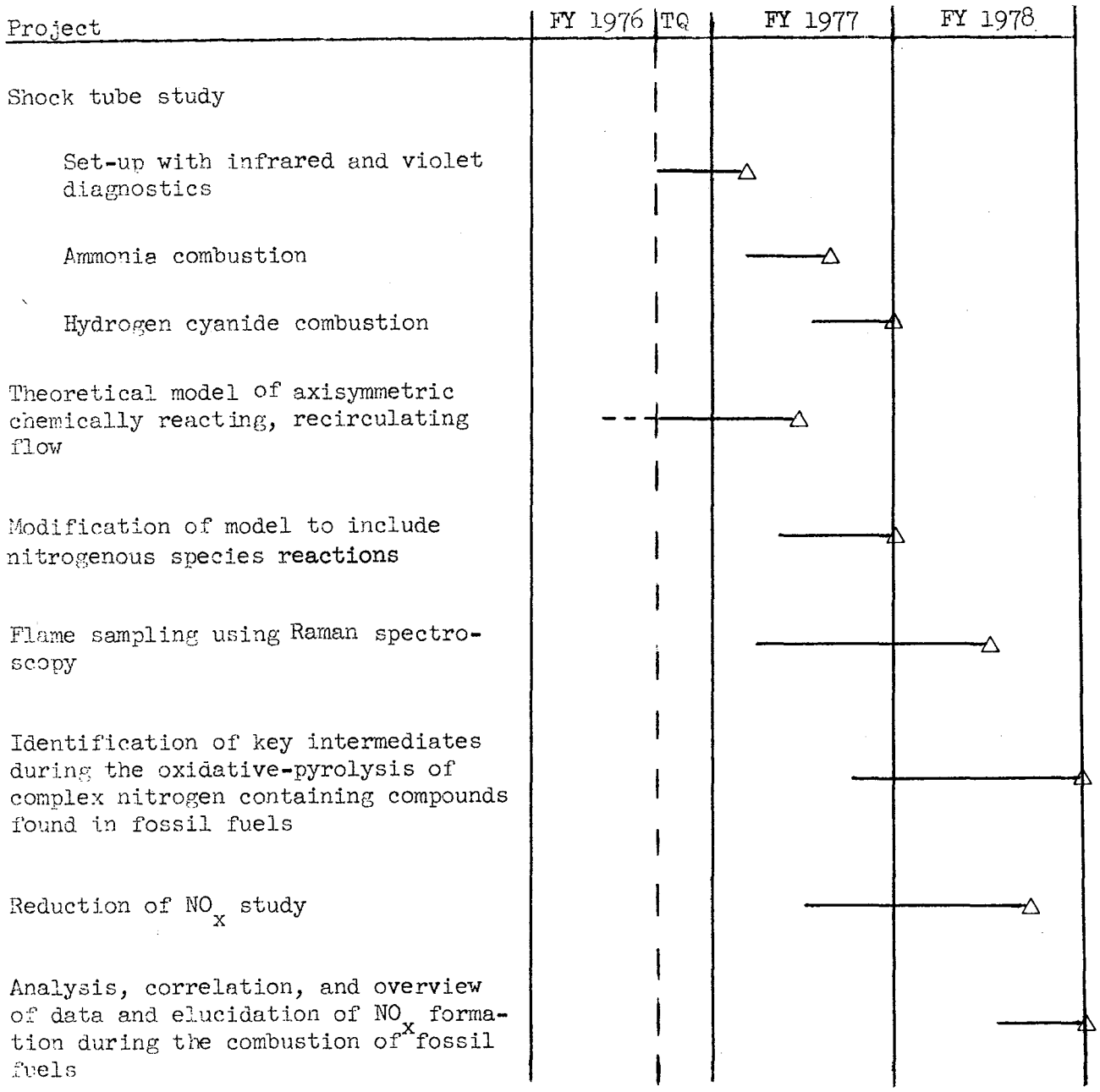
PROGRAM TASK AND SCHEDULE

Owing to the extensive nature of the proposed program, a two-year technical effort is scheduled. The first year will be devoted to characterizing the combustion of ammonia and of hydrogen cyanide. The development of the theoretical model of axisymmetric, chemically reacting, recirculating flows is near completion and the model should be ready for modification to include the reactions of the nitrogenous species as soon as the mechanisms and rate data are available. Actual flame probing should commence by the middle of the first year. Nitrogen oxide reduction studies should also be underway by this time.

Studies concerned with the interaction of NO with NH_3, HCN and CO should begin by the beginning of the second year. The task of identifying key intermediates during the oxidative-pyrolysis of the more complex nitrogen-containing fuels should also begin by the beginning of the second year. The last quarter of the two-year effort will involve a complete analysis of the results and quantitative evaluation of the fate of chemically-bound nitrogen in all environments characteristic of fossil fuel combustion.

Table VI presents the approximate time-scales of the major projects.

TABLE VI. APPROXIMATE TIME-SCALE OF MAJOR PROJECTS



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