FOSSIL ENERGY

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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

Progress Report for the Period
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OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollutants. 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 quinoline, 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. HCN and vinylcyanide, 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 and gas chromatographic monitoring of products and reactants as well as chemiluminescent and specific ion electrode measurements will be used to obtain the data.

SUMMARY OF PROGRESS

Task 1. A rate equation for the oxidation of pyridine in the temperature range of 948 - 1048 K and for both fuel lean and rich mixtures has been developed to describe the data previously reported. The rate appears to be first-order in oxygen and half-order each in pyridine and oxygen consumed, indicating catalysis by product(s). The Arrhenius parameters are 46,800 kcal/mole and 13.4 for E_a and log A (in l/mole · sec) respectively. Measurements of the products indicated at all temperatures, from 948 - 1273 K, that HCN was the major (and only significant) volatile product containing nitrogen for fuel rich mixtures. However, only at 1273 K were there large amounts of NO produced from fuel lean mixtures; at 1173 K and below only very small yields of NO, about 1% or less, were found. The papers on pyridine pyrolysis kinetics were revised and resubmitted to the journal.

Task 2. A paper describing the rate of oxidation of cyanogen and the products formed from the reaction in the range of 1223 - 1323 K was prepared and submitted to Combustion and Flame.

DETAILS OF TECHNICAL PROGRESS

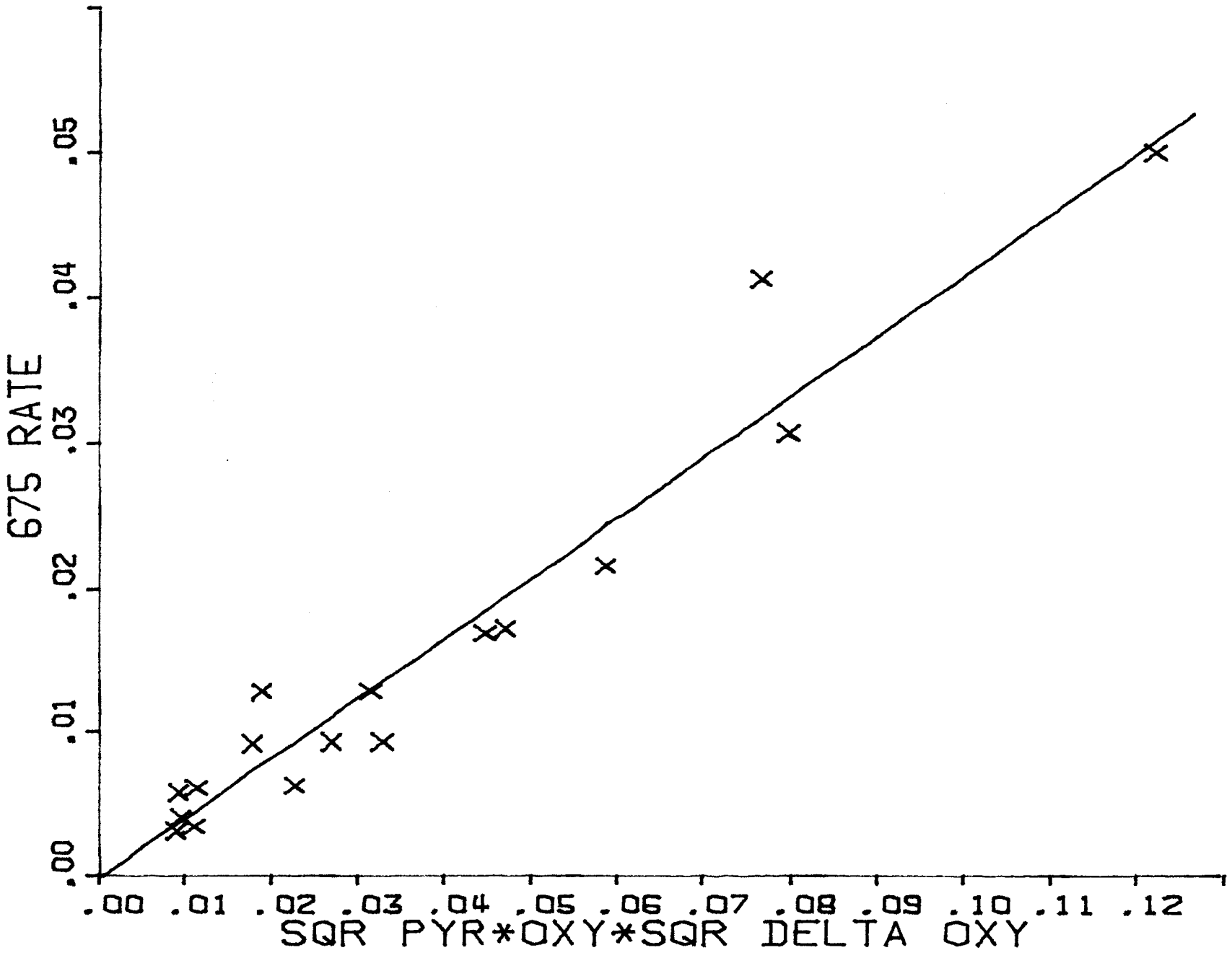
Task 1

The rate of oxidation of pyridine was measured and the complete data were summarized in the preceding report (1). The ranges of conditions for these measurements were: temperature 948 - 1048 K, 1/4 - 2 mole % pyridine, 1 - 7 mole % oxygen and molar ratios of 28 - 0.5 oxygen/pyridine (stoichiometric is 6.25 assuming CO_2, H_2O and N_2 as prpducts), reaction times of 1/4 - 8 sec. It was observed that the rate was weakly dependent on pyridine concentration and strongly dependent on oxygen concentration. However, although the rate increased with initial oxygen concentration, it did not decrease rapidly as oxygen was consumed, indicating some catalysis by oxygen related product(s).

It was found that unless a factor involving oxygen consumed (or initial oxygen concentration) were included in the rate equation, stratification of the data points occurred, according to initial oxygen concentrations. To date the best representation of the data is given by the equation

$$\text{rate} = k_o + k_1 (C_5H_5N)^{\frac{1}{2}} (O_2) (\Delta O_2)^{\frac{1}{2}}$$

where (ΔO_2) is the concentration of oxygen consumed. The constants are summarized in the Table listing the values with their standard deviations, the correlation coefficients and the number of data points. The figures show plots of these data at the five temperatures. It can be readily seen that the intercepts are essentially zero at three of the five temperatures and close to zero for the other two. It has been assumed that k_o is zero for all temperatures and the corrected k_1 values at 973 and 998 were calculated on that basis. The Arrhenius parameters were calculated using the corrected values, although the E_a and A factor were not significantly different using only the least squares values. Work will continue on attempting to find better mathematical representations of the data. After an accurate rate equation has been developed, it should be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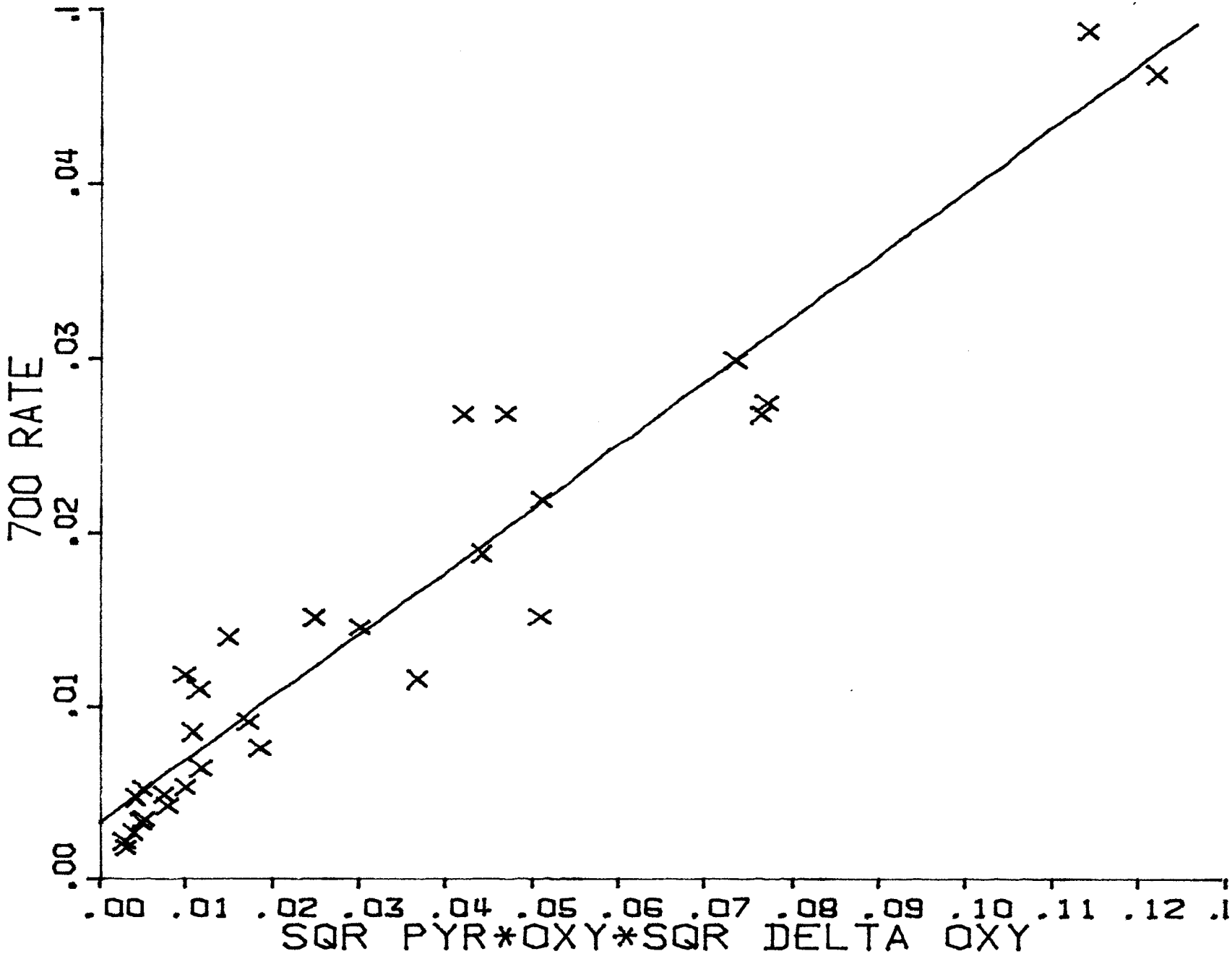
SQR PYR*OXY*SQR DELTA OXY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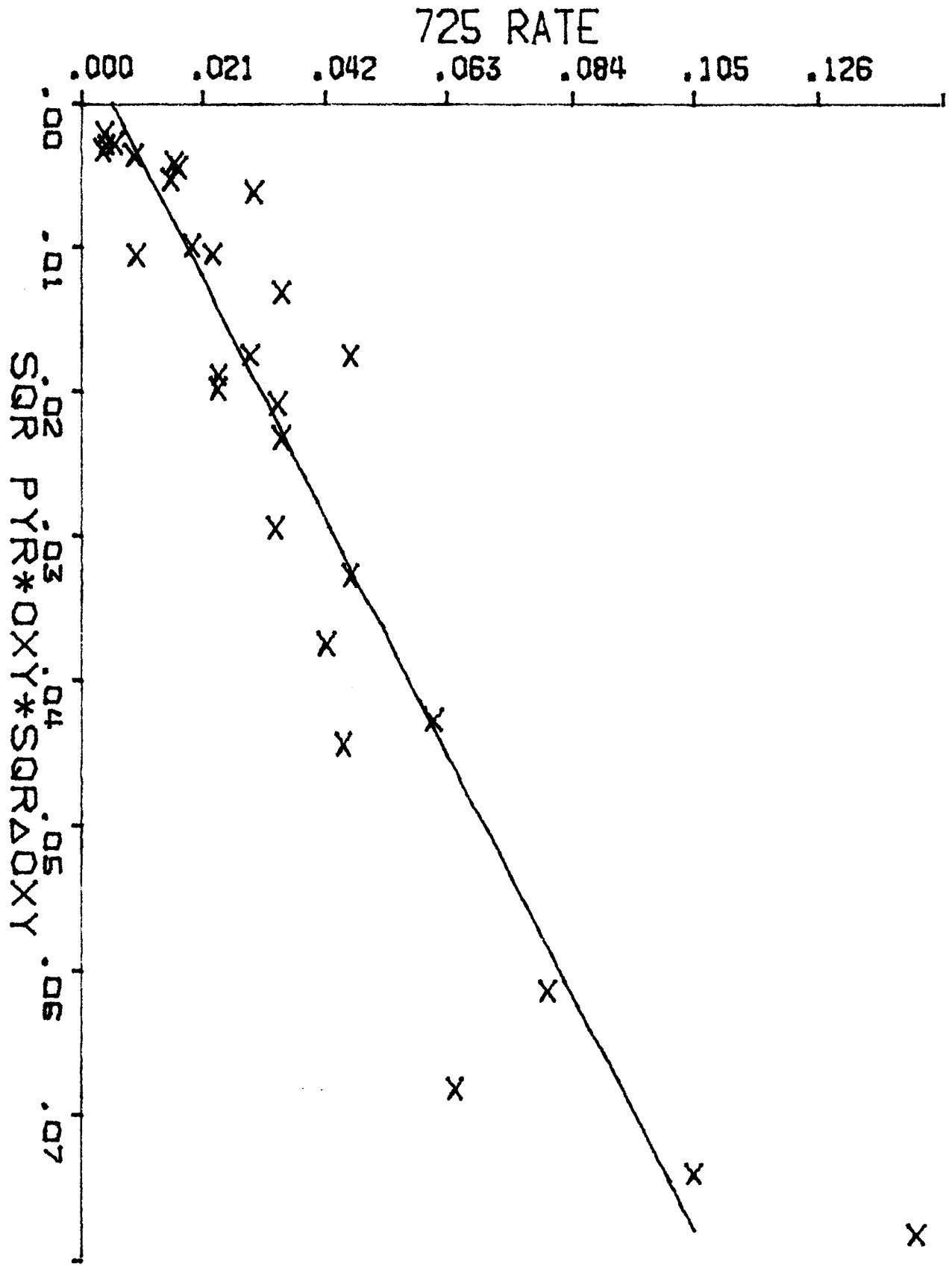
SQR PYR*OXY*SQR DELTA OXY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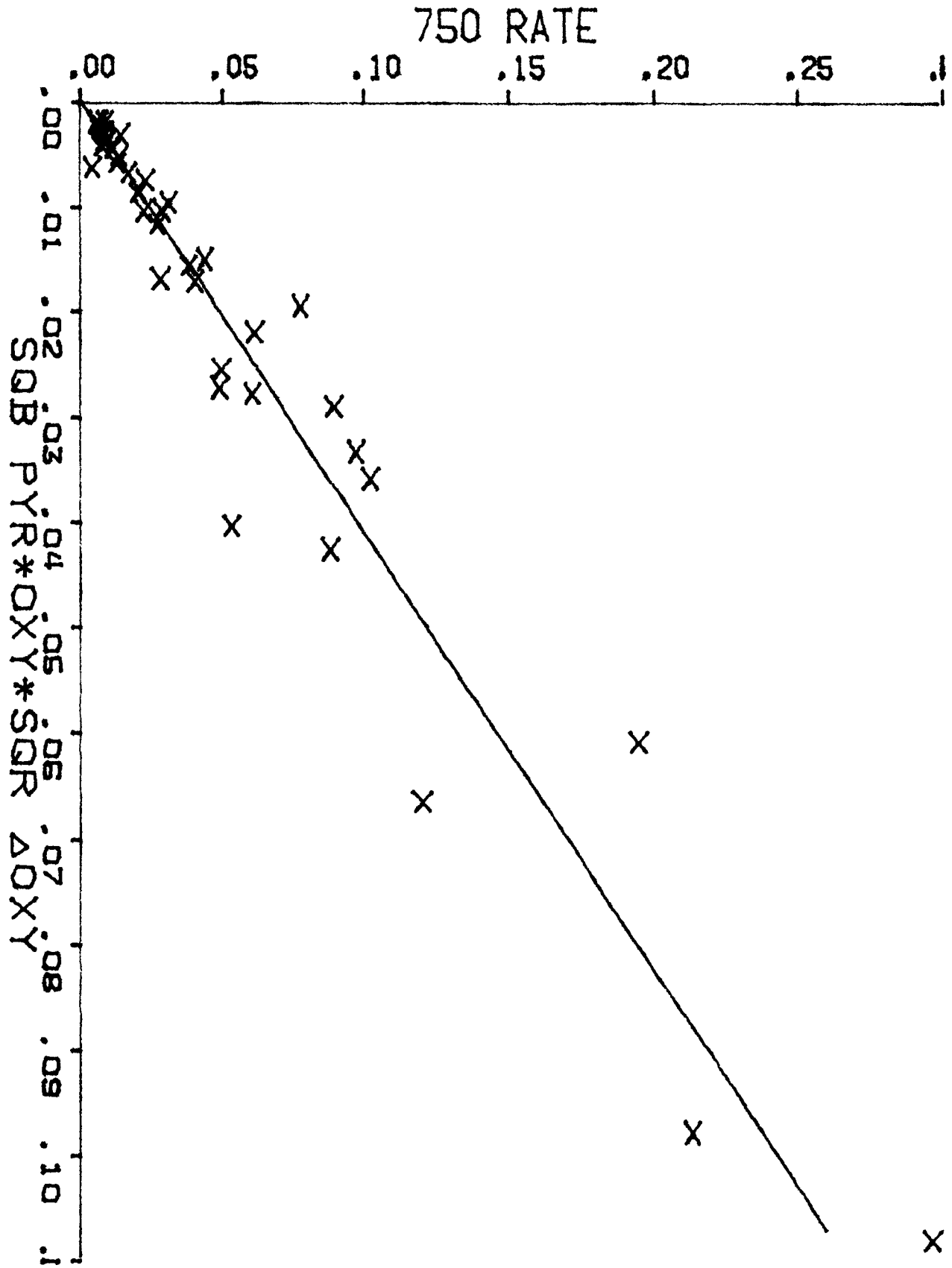
SQR PYR*OXY*SQR∆OXY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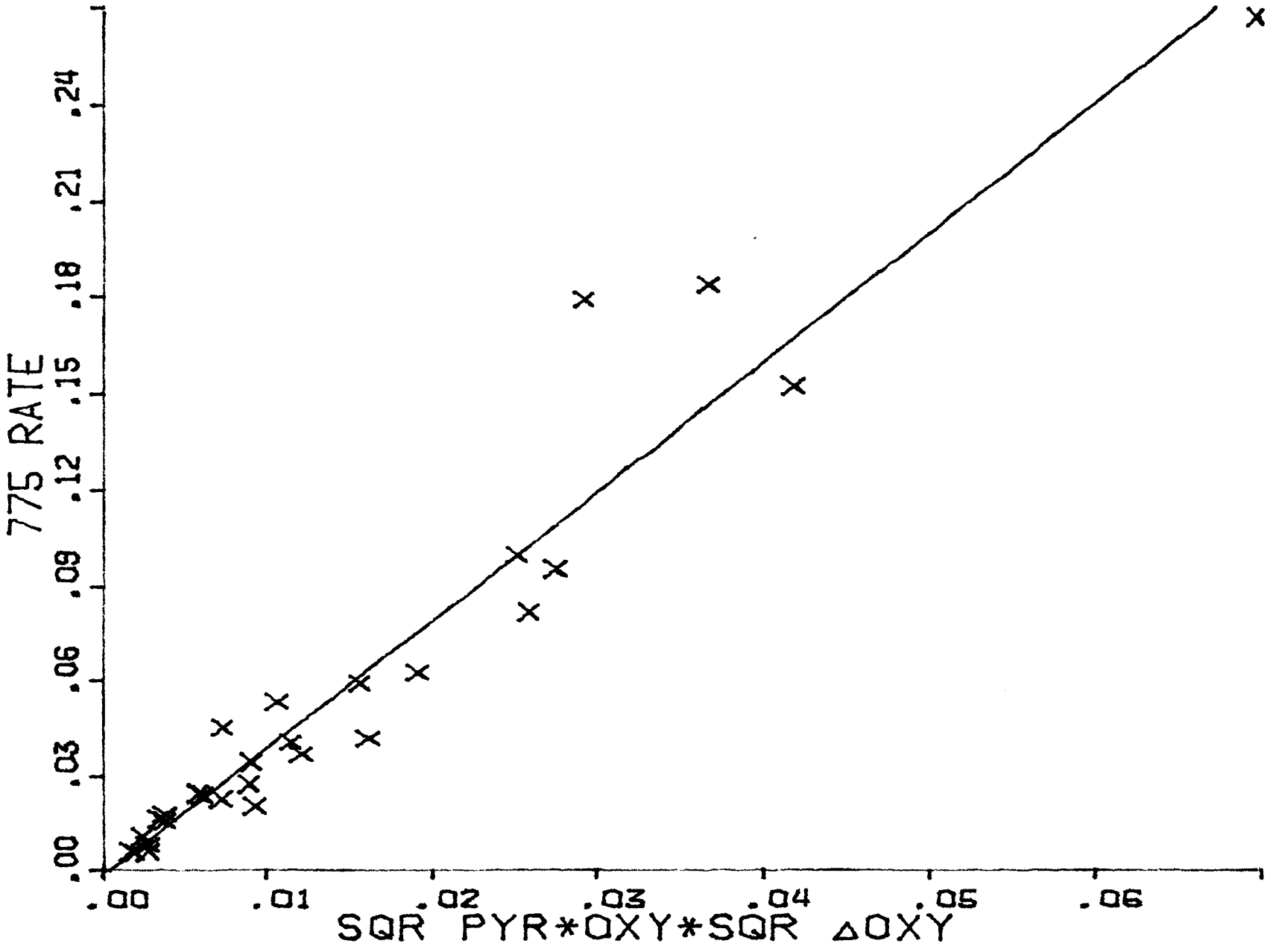
SQRT PYR*OXY*SQRT AOXY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possible to predict the rates at temperatures where they are too high to measure but where the NO formation is found (above 1173 K).

Rate Constants

Temperature K	$k \times 10^6$ (mole/l·sec)	k (l/mole·sec)	Cor. Coef.	Data Pts.
948	-0.2 ± 1.3	418 ± 27	.97	17
973	3.3 ± 0.9	363 ± 20 (614 ± 44)*	.96	31
998	5.4 ± 3.3	1280 ± 100 (1910 ± 180)*	.93	28
1023	0.7 ± 3.3	2430 ± 110	.96	41
1048	-1.7 ± 4.7	4040 ± 220	.96	28

$E_a(k_1)$ 46800 ± 5600 (kcal/mole)

log A (k_1) 13.4 ± 1.2

*Corrected values assuming zero intercepts.

Several experiments were conducted to determine the evolution of NO and HCN using the chemiluminescent analyzer and ion specific electrode, respectively, over a wide range of temperatures. Because the methods were just being developed the quantitative results are not too reliable but the relative information is indicative of what is to be expected. Six HCN determiniations at 948 - 1048 K and with fuel rich mixtures indicated that as the temperature increased the HCN yield also increased, ranging from about 30 to 75%. Two NO determinations indicated for fuel lean mixtures that a negligible amount of this product was formed (less than one %) at 998 and 1023 K. Five experiments at 1273 K indicated large yields of NO for fuel lean mixtures and large yields of HCN for fuel rich mixtures. Four experiments at 1173 K gave the same results for the fuel rich mixtures, however, those that were fuel lean produced only small amounts of NO. These conditions will be investigated more thoroughly later.

The two papers discussing the pyrolysis kinetics of pyridine submitted to the International Journal of Chemical Kinetics were revised in accordance to the referees' suggestions and resubmitted to the journal.

Task 2

A paper describing the oxidation of cyanogen in the temperature range of 1223 - 1323 K was prepared and submitted to Combustion and Flame. The kinetic (2,3) and product (4) data were reported previously and the implications of these results on the mechanism of formation of NO from fuel nitrogen were discussed.

REFERENCES

1. T. Houser, "Fundamentals of Nitric Oxide Formation in Fossil Fuel Combustion", FE-2018-14, Period, June - Sept. 1979.

2. T. Houser, Ibid, FE-2018-3, December 1975 - March 1976.

3. T. Houser, Ibid, FE-2018-5, June - Sept. 1976.

4. T. Houser, Ibid, FE-2018-8, March - June 1977.