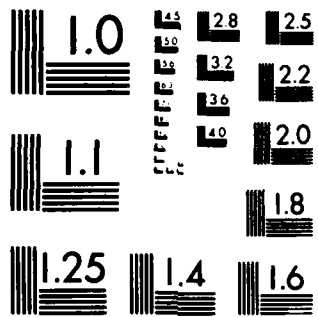END
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A Mechanistic Study of Nitromethane Decomposition

on Ni Catalysts

Final

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AFOSR 82-0099

OCTOBER 1982

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SIGNIFICANCE OF THIS RESEARCH TO THE AIR FORCE

The research conducted under this grant was directed at understanding the fundamentals of nitromethane decomposition over nickel catalysts to evaluate the potential of further development of nitromethane as a monopropellant. This study addressted two questions:

1) May the kinetics of nitromethane decomposition be altered by choice of catalyst material to allow light-off at lower temperatures?

2) May the problem of carbon deposition be alleviated by an appropriate choice of fuel?

With respect to the question of catalytic activity this study clearly showed that catalytic activity may be enhanced by finding materials which severely weaken the N-O bonds in nitromethane upon adsorption. On Ni catalysts it was found that as the oxidation of the surface increased the strength of the nitromethane adsorption decreased and the activation barrier for decomposition increased.

The problem of catalyst poisoning by carbon deposition should be solvable by an appropriate choice of monopropellant mixture. Carbon deposition was found to occur by the secondary reaction of HCN decomposition; carbon deposition should not occur if an oxidant rich propellant was mixed with nitromethane to oxidize the carbon. A mixture of nitroform and methane would be an appropriate fuel mixture providing it could be stabilized against shock detonation without making it fuel rich.

INTRODUCTION

Nitromethane is one of several compounds which decomposes exothermically and may be used as a monopropellant in small rocket thrusters and demand gas generators. The use of nitromethane for such uses has not received much attention due to the absence of an appropriate catalyst to facilitate its decomposition. Recently, the decomposition of nitromethane over NiO and Cr_2O_3 catalysts has been examined to examine the feasibility of a nitromethane-based monopropellant system (1, 2). These studies indicated that a NiO/alumina catalyst was effective in causing nitromethane decomposition. However, relative to existing hydrazine based monopropellant systems the nitromethane-NiO/alumina system suffered two severe drawbacks; first, it required much higher light-off temperatures than hydrazine based systems, and second, the decomposition reaction poisoned the catalyst with carbon degrading performance with continued use.

We have undertaken studies to examine the mechanism and kinetics of nitromethane decomposition over well defined Ni catalysts. These studies have shown that the catalyst activity for nitromethane decomposition is dependent on the level of oxidation of the nickel. It has also been shown that carbon poisoning of the catalyst is due to a secondary reaction and should be controllable by making appropriate monopropellant mixture.

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EXPERIMENTAL PROCEDURE

The decomposition of nitromethane on a Ni(111) surface and an oxidized Ni(111) surface was studied in a stainless steel ultrahigh vacuum chamber. The chamber was pumped by ion and titanium sublimation pumps to a base pressure of 3×10^{-10} torr. The system was equipped with 4-grid LEED optics, glancing incidence electron gun, quadrupole mass spectrometer, Argon ionization source, gas manifold with variable leak valves, and a rotatable sample manipulator. The Ni(111) crystal was heated by radiation from a tungsten filament located in back of the crystal, crystal cooling to 250 K was accomplished by thermal conduction to a liquid nitrogen reservoir; temperature was monitored by chomel alumel thermocouple spotwelded to the back of the crystal.

The structure and composition of the Ni(111) surface was verified by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). A clean Ni(111) surface was prepared by Argon sputtering and high temperature annealing. The clean surface showed less than 0.02 monolayers of impurities. Well defined adlayers Ni(111)-p(2×2)C, Ni(111)-p(2×2)O and Ni(111)-p(2×2)S were prepared as verified by LEED and correlated with AES for use as calibration points for surface coverages of adlayers.

Nitromethane obtained from Eastman Chemicals and deuterated nitromethane (> 99% D) obtained from Sigma Scientific were used as received. Mass spectra were verified to check sample purity. They were cooled in an ice water bath to give a vapor pressure of 2000 millitorr. The Ni crystal was exposed to a beam of nitromethane effusing from a 0.25 mm ID tube with a backing pressure of 100-2000 millitorr. Effective fluxes at the crystal surface equivalent to 10^{-8} to 10^{-2} torr were obtained while the system pressure was kept below 5×10^{-9} torr.

EXPERIMENTAL RESULTS

Nitromethane was found to readily adsorb on a Ni(111) and a Ni(111)-p(2×2)O surface at temperatures below 300 K; the sticking probability was greater than 0.2 up to near saturation coverage. The nitromethane adsorbed molecularly and decomposed above 350 K as shown in Figure 1. On clean Ni(111) nitromethane decomposed at 370 K to primarily HCN, H_2 and adsorbed oxygen. Lesser amounts of N_2, H_2O, NH_3, and adsorbed carbon and nitrogen were also formed in the initial decomposition step at 370 K. Subsequent surface reactions led to the desorption of CO, CO_2, N_2 and NO at temperatures that corresponded to atomic recombination reactions; CO and CO_2 desorbed at 550 K, N_2 at 625 K and NO at 650 K. These gas phase species were all identified by their fragmentation patterns in the mass spectrometer. Table I lists the combinations of frag- ments to identify the various products. Adsorbed atomic products were moni- tored by AES; Figure 2 shows a series of Auger spectra tracing out the reac- tion sequence.

The reaction sequence on Ni(111)-p(2×2)O was identical to that observed on clean Ni(111) but the decomposition step occurred at 420 K, about 50 K above the peak temperature on the clean surface. The reaction of nitro- methane on a heavily oxidized Ni(111) surface was also attempted. A Ni(111) surface oxidized to the level of approximately 1 monolayer of oxygen as determined by AES (ca. a Ni(111)-p(2×2)O surface has 0.25 monolayers of oxygen) was exposed to nitromethane. At a temperature of 250 K, which was the lowest temperature obtainable, no nitromethane adsorption was detected.

The kinetics of nitromethane decomposition were examined on the Ni(111) and Ni(111)-p(2×2)O surfaces by means of coverage and heating rate variations.

The coverage variation study shown in Figure 3 indicated unusual kinetics.
The peak temperature for the initial decomposition step was found to shift
to higher temperature with increasing nitromethane coverage. In addition the
peak width decreased as the peak shifted to higher temperatures, with unuusally
narrow desorption peak widths of 11°K at saturation coverage. This behavior
is indicative of attractive interactions between adsorbed surface intermediates
(3). The activation energy for the decomposition reaction was determined for
saturation coverage of nitromethane by heating rate variation (4). In the
presence of adsorbate interactions this method yields an effective activation
energy which is the sum of the activation energy for surface reaction and the
interaction energy between adsorbed species. In order to obtain the values
of the activation energy and interaction energy the activation energy was
determined from peak shape analysis at low surface coverage where adsorbate
interactions were not significant. The low coverage data was also used to
determine the pre-exponential factor for surface reaction. The rate data on
the two surfaces was fit by rate expressions of the form

$$- \frac{d\theta_{CH_3NO_2}}{dt} = \nu \, \theta_{CH_3NO_2} \, \exp(-(E-\omega)/RT)$$

where $\theta_{CH_3NO_2}$ is the surface coverage of nitromethane

           ν is the pre-exponential factor

           E is the activation energy

           ω is the interaction energy.

The kinetic parameters found are listed in Table II. These rate parameters
were checked by comparing the experimental temperature programmed desorption
curves with theoretical desorption curves generated from the rate expression
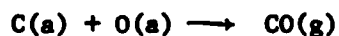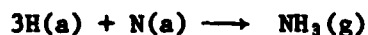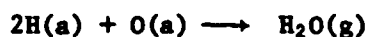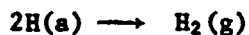above. The deviations were not significant indicating that the kinetic

parameters shown in Table II gave an excellent fit to the experimental data.

In an attempt to determine what the rate limiting step in the decomposition was the decomposition of CD_3NO_2 was examined. The deuterated nitromethane decomposed to DCN and D_2 at 370 K on Ni(111) with the same narrow peak widths found for CH_3NO_2. These results indicated that the rate limiting step in the decomposition did not involve the breaking of a C-H bond.

DISCUSSION

The results from this study agree nicely with the previous study of nitromethane decomposition over NiO/alumina catalysts (2). In that study it was proposed that nitromethane adsorbed molecularly and that the rate limiting step in the decomposition was N-O bond scission. The decomposition over the Ni(111) catalyst clearly showed HCN as the primary reaction product indicating that the C-N bond was not broken in the decomposition step. These results may be compared to the gas phase decomposition of nitromethane where C-N bond rupture is the initial step in the decomposition reaction (6). In the gas phase the major reaction products were NO, H_2O, CO and CH_4; none of these products was formed in significant quantities by heterogeneous catalytic reaction.

The reaction mechanism suggested by this study for the decomposition of nitromethane over nickel and nickel oxide catalysts is shown below.

$$CH_3NO_2(g) \longrightarrow CH_3NO_2(a)$$

$$CH_3NO_2(a) \longrightarrow HCN(a) + 2H(a) + 2O(a)$$

$$HCN(a) \longrightarrow HCN(g)$$

$$HCN(a) \longrightarrow H(a) + C(a) + N(a)$$

$$2H(a) \longrightarrow H_2(g)$$

$$2H(a) + O(a) \longrightarrow H_2O(g)$$

$$3H(a) + N(a) \longrightarrow NH_3(g)$$

$$2N(a) \longrightarrow N_2(g)$$

$$C(a) + O(a) \longrightarrow CO(g)$$

$$C(a) + 2O(a) \longrightarrow CO_2(g)$$
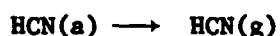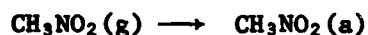
Initially the nitromethane adsorbs on the nickel surface. It seems reasonable to expect that the nitromethane probably bonds to the surface via the oxygens. Reflection infrared studies now in progress show weakening of the N-O bonds and the molecule to be oriented with both oxygens toward the surface as shown below (7)

$$
\begin{array}{c}
- O \\
\quad\quad N - CH_3 \\
- O
\end{array}
$$
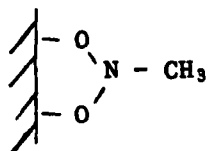
The nitromethane subsequently reacts by breaking of the nitrogen oxygen bonds. Both oxygen bonds appear to be broken as no NO, NO_2, or CH_3NO products were detected. The rate limiting step seems to clearly correspond to N-O bond scission, as the only bonds breaking were N-O bonds and C-H bonds and the absence of a kinetic isotope effect for CD_3NO_2 seems to rule out C-H bond scission as important in the rate limiting step. Hydrogen desorbed simultaneously with HCN as hydrogen recombination is an extremely fast reaction at temperatures above 350 K.

The formation of N_2, NH_3 and adsorbed carbon and nitrogen indicated that some of the HCN product must have further decomposed. The desorption of N_2 at the initial decomposition also indicates that the HCN decomposition goes through reactive precursors and does not yield adsorbed atomic species directly. The combined use of AES and TPD shows how the adsorbed atomic species (C, N, O) react to yield CO, CO_2, N_2 and NO. The adsorbed carbon is a surface carbide which has been found to react with adsorbed oxygen at 550 K to yield CO and CO_2. The carbide form of the carbon is evident from the AES which shows a three peak structure characteristic of metal carbides (8). The nitrogen reacted at 625 K to form N_2 with a small amount of NO detected

at 650 K. The clean Ni(111) surface showed an oxygen buildup on the surface after the carbon and nitrogen had desorbed as shown in Figure 2.

The oxidation of the surface by nitromethane decomposition is contrary to previous results where catalyst poisoning occurred due to carbon deposition. This apparent discrepancy is due to the fact that secondary reactions involving the decomposition of the HCN were minimal in the UHV studies reported here, hence the hydrogen and carbon were not oxidized. This resulted in the oxygen on the surface not being reduced as it was in the case of the higher pressure reactions where the secondary reactions were important. This effect was evident in comparing NiO/alumina and Cr_2O_3/alumina catalysts where the NiO catalyst yielded less HCN product and was poisoned faster than the Cr_2O_3 catalyst (2).

The present study also indicated that surface oxidation played an important role in the kinetics of the nigromethane decomposition. The activation energy for the surface reaction was found to increase in going from the Ni(111) to the Ni(111)-p(2×2)O surface. This increase in activation energy can be attributed to weaker bonding of the nitro group oxygens to the surface when the adsorbed oxygen is tying up some of the metal electrons. Increasing the amount of ad- sorbed oxygen weakens the adsorption of the nitro group leaving the N-O bonds stronger and hence the activation energy increased. When the surface became too heavily oxidized the activation energy for decomposition was greater than the enthalpy of adsorption hence the nitromethane desorbed before it decomposed, so we were able to detect any reaction. This supposition is further supported by previous studies on NiO/alumina catalysts which found the activation energy for decomposition was almost twice the enthalpy of adsorption (2).

The kinetics observed for nitromethane decomposition on the Ni(111) and Ni(111)-p(2×2)O surface are somewhat unusual. The TPD results seem to indicate

attractive interactions between adsorbed intermediates, and the data can be fit
very closely with such a model. There are previous surface science studies
which have also observed this same type of kinetics (3, 9). The previous cases
where such kinetics were observed are similar to the present case in that the
adsorbed species were highly polar molecules. It thus seems reasonable to
attribute the attractive interactions to alignment of the molecular dipoles
of the nitromethane molecules on the surface. Further studies using reflection
infrared spectroscopy should be helpful in more clearly defining the le of
such interactions.

CONCLUSIONS

The decomposition of nitromethane was studied on Ni(111) and oxidized Ni(111) surfaces. It was found that the strength of nitromethane adsorption decreased with increasing oxidation of the surface and the activation energy for decomposition increased. The nitromethane decomposed by N-O bond scission yielding HCN and H_2 as the major reaction products. Additionally some HCN decomposed to adsorbed carbon and nitrogen. The kinetics for nitromethane decomposition indicated attractive interactions between adsorbed species, causing the reaction rate to decrease with increasing surface coverage.

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TABLE I

Mass Fragments Used for Product Identification

Compound	Mass Fragments
H_2	2
NH_3	17
H_2O	18
HCN	27
N_2	28 and 14
CO_2	28 and no 14
NO	30
CO_2	44
CH_3NO_2	61

TABLE II

Kinetic Parameters for Nitromethane Decomposition

	Ni(111)	Ni(111)-p(2×2)O
Activation Energy-E (kJ/mole)	115	125
Interaction Energy-ω (kJ/mole)	$- 5$	$- 5$
Pre-exponential Factor (S^{-1})	10^{16}	10^{16}

FIGURE CAPTIONS

Figure 1 - Product desorption spectra for nitromethane decomposition on Ni(111).

Figure 2 - Auger spectra for nitromethane decomposition on Ni(111)

     a)   clean Ni(111) before CH_3NO_2 adsorption

     b)   after CH_3NO_2 adsorption and heating to 450 K

     c)   after heating to 575 K

     d)   after heating to 800 K

Figure 3 - Coverage variation study of nitromethane decomposition on

NI(111)-p(2×2)O

     a) $\theta = \theta_{sat}$

     b) $\theta = 0.45\,\theta_{sat}$

     c) $\theta = 0.30\,\theta_{sat}$

     d) $\theta = 0.20\,\theta_{sat}$

     e) $\theta = 0.10\,\theta_{sat}$
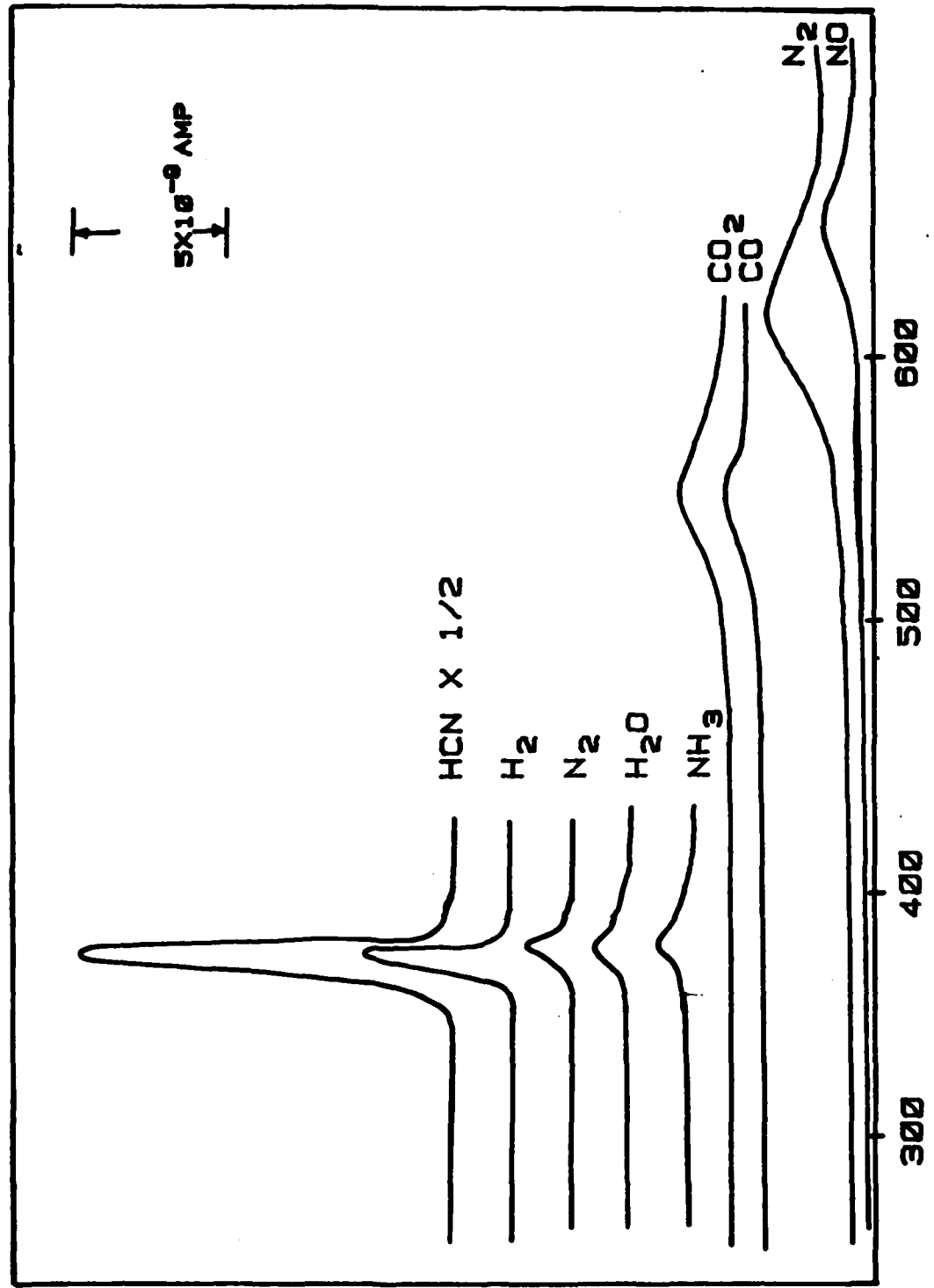
NITROMETHANE DECOMPOSITION

Fig. 1

MASS SPECTROMETER CURRENT

TEMPERATURE (°K)

AES OF DECOMPOSITION PRODUCTS
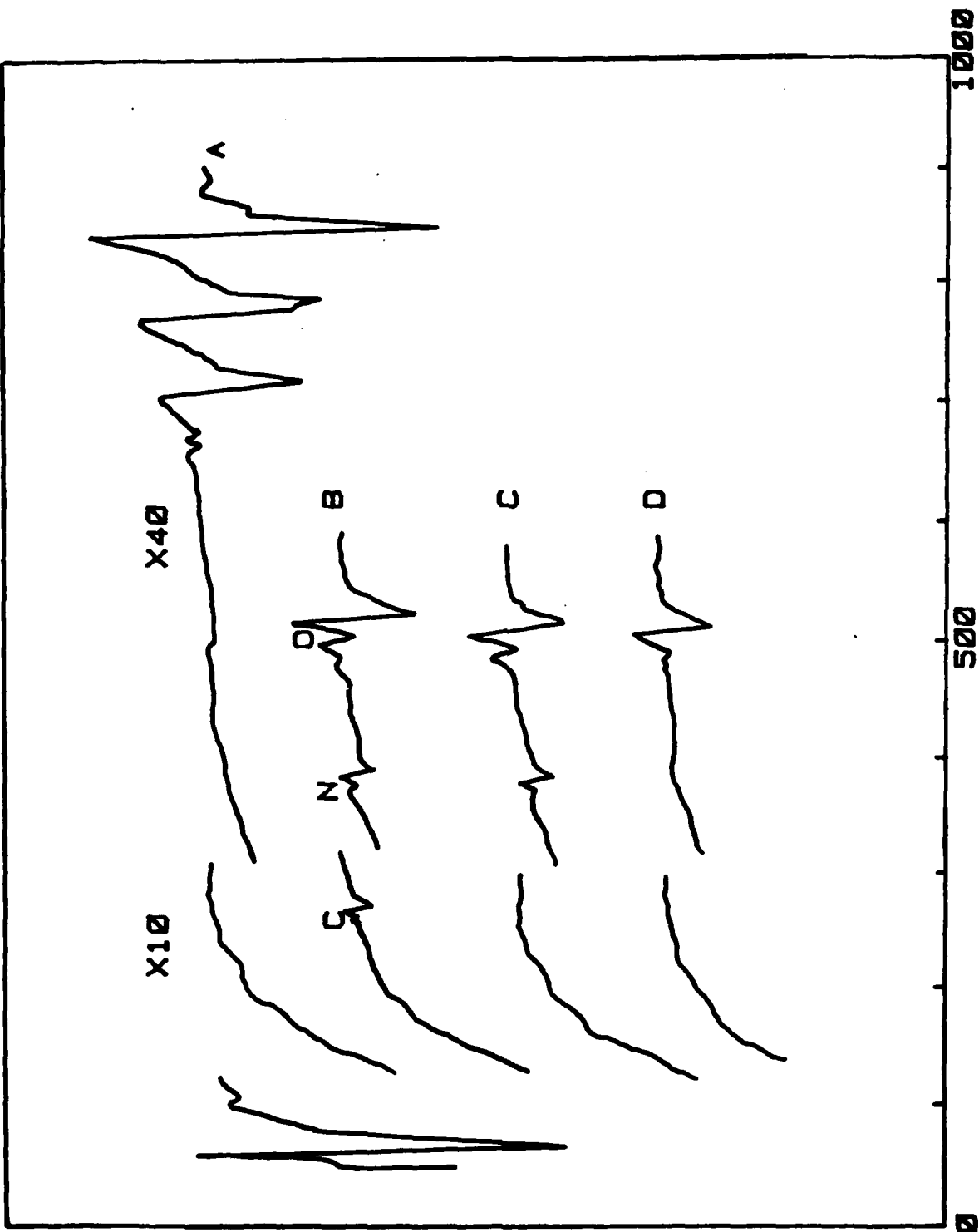
ELECTRON ENERGY (VOLTS)

Fig. 2

HCN/CH$_3$NO$_2$ COVERAGE VARIATION

TEMPERATURE (°K)
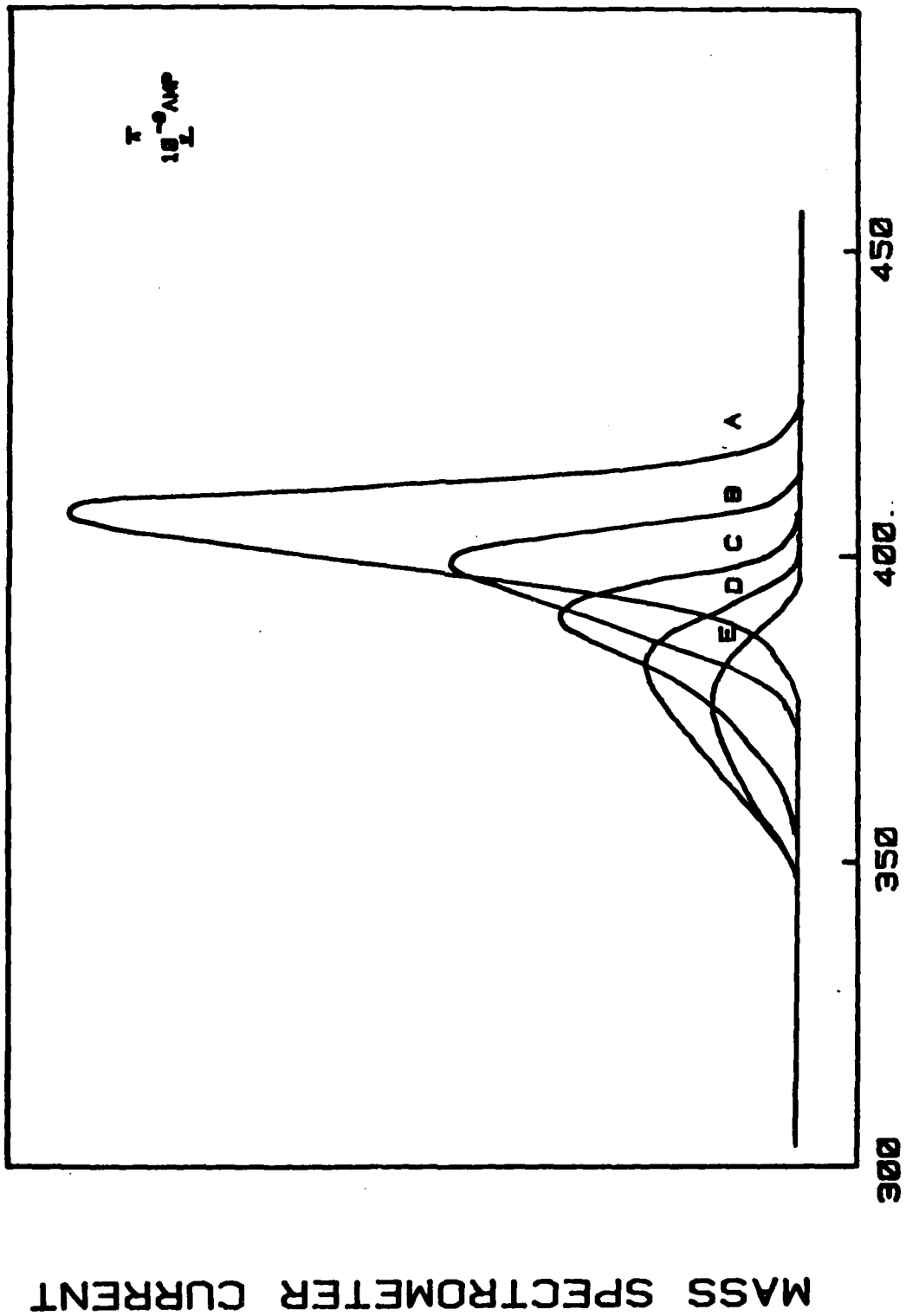
MASS SPECTROMETER CURRENT

Fig. 3

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A MECHANISTIC STUDY OF NITROMETHANE DECOMPOSITION ON NI CATALYSTS	Final
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Jay Benziger	AFOSR-82-0099

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Department of Chemical Engineering Princeton University Princeton, NJ 08544	61102F 2303/D9

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Air Force Office of Scientific Research/NC Building 410 Bolling AFB, DC 20332	October 1982
	13. NUMBER OF PAGES
	19

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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monopropellant
nitromethane
nichel catalysis
catalyst poisoning

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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