THE EFFECT OF NITRIC OXIDE ON THE PYROLYSIS OF ETHANE

by

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PREFACE

Studies of the pyrolysis of organic substances in the presence of nitric oxide were originally carried out with the object of studying the unimolecular decompositions of molecules. It was believed that addition of a sufficient amount of nitric oxide would suppress all of the free-radical reactions which normally take place in the absence of NO. Any residual reaction would hence correspond to a molecular reaction. Later it became increasingly evident that radical reactions do still take place irrespective of the concentration of nitric oxide. The role of nitric oxide, however, remained a puzzle. The present work was undertaken to evaluate the function of nitric oxide.

This research was conducted under the direction of Prof. K. J. Laidler, whose patience and constant readiness for valuable discussions is most gratefully acknowledged. With gratitude the author wishes to thank Dr. M. H. Back for many helpful suggestions concerning experimental problems. The author is also indebted to the Ontario Government for the award of Ontario Graduate Fellowships.

Finally, last but not least, thanks are due to my colleagues for many useful discussions during these years.

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ABSTRACT

The pyrolysis of ethane inhibited by nitric oxide has been investigated at temperatures ranging from 550 to 596° C by gas-chromatographic analysis. Mixtures of C_2H_6-NO ranged from 1.6 to 62 % NO. The rates of production of the primary products ethylene, hydrogen, methane, nitrogen, water, nitrous oxide and acetonitrile were measured under varying experimental conditions. Hydrogen cyanide, carbon monoxide, acetaldehyde, n-butane, butene-1, cis- and trans-butene-2, and butadiene-1,3 were detected as secondary products and occasionally measured.

It was found that nitric oxide decomposed extensively with a finite initial rate. The consumption of NO was determined directly and a good mass balance was obtained.

The orders of the rates of formation with respect to ethane and nitric oxide were determined for all primary products at 596° C. The activation energies for the production of all primary products were determined for two different C_2H_6-NO mixtures in the temperature range 550 to 596° C. Except for the production of water and nitrogen the activation energies were found to depend on the composition of the mixture.

A mechanism is proposed which gives good agreement with experiment. The main points of the mechanism are:

(i) Initiation takes place mainly by unimolecular decomposition of ethane.

(ii) Nitric oxide scavenges ethyl radicals to form acetaldoxime which decomposes, thereby replacing in essence the reaction

$$C_2H_5 \longrightarrow C_2H_4 + H$$

to a large extent by

$$C_2H_5 + NO \longrightarrow C_2H_4N\cdot + OH.$$

In this way the C_2H_5 radical causes the decomposition of nitric oxide.

(iii) Termination takes place mainly by unimolecular decomposition of acetaldoxime to inactive products.

Reactions are proposed to account for the formation of the secondary products observed. Some of the relevant rate parameters are evaluated. An interpretation is given of the rate measurements previously performed by means of pressure measurements.

Chapter I

INTRODUCTION

I. Historical Review

A. Early Work

The pyrolytic work involving organic substances and nitric oxide developed from an attempt to study the catalytic effects of nitric oxide on the pyrolysis of diethyl ether (1). Instead of a simple catalysis, Staveley and Hinshelwood found that small amounts of NO had an inhibiting effect. Catalysis, however, was observed at high NO concentrations. It was also found that at least part of the nitric oxide disappeared to give nitrogen in what the authors thought were side reactions.

In further studies Staveley and Hinshelwood (2, 3, 4, 5) observed that small amounts of NO had an inhibiting effect on the thermal decomposition of many other organic substances. They attributed this effect to the ability of NO to suppress chains by removing free radicals from the system. The limiting rate was thought to represent a chain-free primary process.

The inhibition of the pyrolysis of ethane by nitric oxide was studied first by Staveley in 1937 (6). He found that the NO was slowly removed in the course of the reaction. The removal was interpreted as being due largely to the ethylene formed in the decomposition. The rate at maximum inhibition was thought to be due to molecular breakdown of ethane into hydrogen and ethylene. Studies leading to similar conclusions were also made with other hydrocarbons (7).

It must be mentioned that the early studies had one important weakness. This was that the experimental techniques at the time did not permit full studies of the formation of all products and of the disappearance of nitric oxide. The common experimental technique was to follow the reaction by measuring the pressure change.

B. Evidence for Radical Chains in the Presence of Nitric Oxide

With the availability of mass spectrometers and deuterated substances it became possible to decide whether radicals took part in the decomposition at maximum inhibition. As early as 1947 Eltenton (8) detected radicals in the inhibited decomposition. He reported that no appreciable decrease in the concentration of methyl radicals was observed. In 1951 Wall and Moore (9) pyrolysed pure C_2H_6 and 50-50 mixtures of C_2H_6 and C_2D_6 in the absence and presence of NO and analysed the products for hydrogen, ethylene, methane and ethane. They found that at 615°C the inhibitory effect of an addition of 5% NO was limited to the first 5 minutes of the reaction. After that time NO itself no longer appeared in the analysis. This suggests that the NO was completely consumed. Moreover, not only did isotopic mixing occur but NO did not even greatly inhibit the isotopic mixing of the methanes and hydrogens. Only the mixing of ethanes was inhibited considerably at higher temperatures. Further work along these lines was performed by Rice and Varnerin (10) and Varnerin and Dooling (11). These authors studied the decomposition of C_2D_6 in the presence of the stable CH_4 and measured the isotopic mixing in the absence and presence of NO in the maximally-inhibited region. The pure C_2D_6 decomposes as follows:

$$C_2D_6 \longrightarrow 2\ CD_3$$
$$CD_3 + C_2D_6 \longrightarrow CD_4 + C_2D_5$$
$$C_2D_5 \longrightarrow D + C_2D_4$$
$$C_2D_6 + D \longrightarrow D_2 + C_2D_5$$
$$2\ C_2D_5 \longrightarrow C_4D_{10} \text{ or } C_2D_4 + C_2D_6$$

In the presence of CH_4 one has the additional reactions:

$$CH_4 + CD_3 \longrightarrow CD_3H + CH_3$$
$$CH_3 + C_2D_6 \longrightarrow CH_3D + C_2D_5$$
$$CH_4 + C_2D_5 \longrightarrow CH_3 + C_2D_5H$$
$$CH_4 + D \longrightarrow HD + CH_3$$

Addition of NO to decomposing C_2D_6 should diminish the amounts of mixed products and mixing should approach zero at maximum inhibition if the molecular hypothesis were true. It was found that NO did not suppress extensive mixing. Although the measurements were only semiquantitative, they definitely established the fact that chain reactions are still taking place in the maximally inhibited region.

It must be mentioned, however, that Hinshelwood and his coworkers disagreed with this conclusion (12). They discounted the results of Rice and Varnerin (10) on the grounds that CH_2 radicals produced in

$$C_2H_6 \longrightarrow CH_2 + CH_4$$

would produce the mixing observed, assuming that the NO does not effectively scavenge the CH_2. They further suggested that deuterium exchange might also occur by mechanisms not involving alkyl radicals. Recent investigations of the pyrolysis of ethane (13, 14, 15) do not support the assumption of CH_2 being present, and Kuppermann and Larson (16), in a careful study of the pyrolysis of mixtures of C_4H_{10} and C_4D_{10} in the absence and presence of NO, showed that mixing by a molecular mechanism does not take place. Their results support the earlier conclusions. Isotopic mixing was also shown to take place in the maximally inhibited decomposition of dimethyl ether (17) and of propane (18). Hence, it can be considered as certain that a molecular mechanism is at best only a very minor mode of decomposition of pyrolyses maximally inhibited by NO.

C. The Fate of RNO

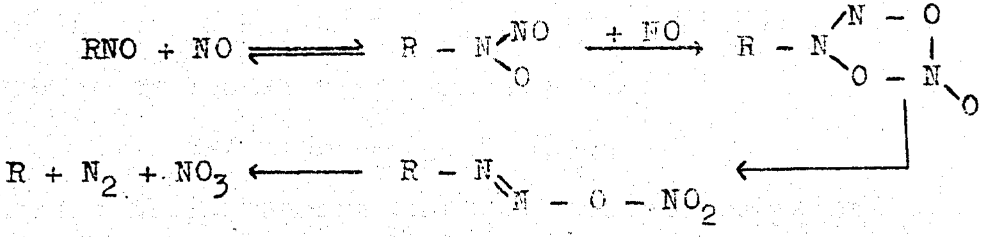
From the very start of NO inhibition studies of pyrolyses it was assumed that chain carriers R react with NO as follows:

$$R + NO \longrightarrow RNO.$$

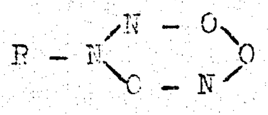
But for a long time the fate of RNO was completely unknown. During the last 20 years a considerable body of evidence dealing with the reaction of alkyl radicals and nitric oxide has accumulated. The first unambiguous production of nitroso methane was reported from the photolysis of tert-butyl nitrite (19). Later the nitroso compounds of all the $C_1 - C_4$ alkyl radicals (20, 21, 22, 23, 24) were detected in pyrolytic systems. For further information on the following discussion the reader is referred to the reviews by Gowenlock (24) and Heicklen and Cohen (25).

1. Radical chain decomposition

RNO can react in various ways. At high NO pressures and low temperatures it has been suggested (26) that RNO reacts as follows:



Later Johnston and Heicklen (27) suggested a sixmembered intermediate:



The most direct and convincing evidence for this type of chain reaction comes from the work of Christie and her coworkers (28, 29, 30, 31, 32). These workers observed and monitored the production of NO_2. They found that the rate of the NO_2-producing reaction was proportional to $[NO]^2$ and the rate of removal of RNO to the first power of $[RNO]$. In all systems studied they found N_2 and NO_2 as products and the rate equations agreed with

$$v_{N_2} = k[RNO][NO]^2.$$

In some cases they observed chain lengths exceeding 100. As Heicklen and Cohen pointed out (25), the evidence for or against this reaction when RNO is HNO is not very convincing. If it occurs, chain lengths must be short.

2. Removal by NO with production of nitrous oxide and alkoxy radicals

Another reaction for which some evidence has been presented by Johnston and Heicklen (27) is

$$RNO + NO \longrightarrow RO + N_2O.$$

Combining their results and some evidence obtained by Christie (28), they deduced

$$k = 8.3 \times 10^3 \left[\exp - 7700/RT\right] \text{ l mole}^{-1} \text{ sec}^{-1} .$$

It seems, however, that more experimental work is needed to establish this reaction with certainty. Recently, in a decomposition study of 2-methyl-2-nitrosopropane - a nitroso compound which cannot isomerize to an oxime - Gowenlock (33) found no evidence for this type of reaction.

3. Addition of radicals

At very low NO concentrations, high radical concentrations and low temperatures it has been found that radicals add to the RN=O bond. According to Lampe and Kohout (34)

$$HNO + H \longrightarrow HNOH$$

$$HNOH + H \longrightarrow H_2NOH$$

and according to Bromberger and Phillips (35)

$$2\ CH_3 + CH_3NO \longrightarrow (CH_3)_2NOCH_3.$$

This was confirmed later by Maschke, Shapiro and Lampe (36, 37).

4. Isomerization of RNO to R'=NOH

The isomerization of the alkyl nitroso compounds to the corresponding oximes was proposed quite early by Mitchell and Hinshelwood (38). Raley, Rust and Vaughan (39) were the first to prove that CH_2NOH could arise from CH_3 and NO at 225° C. Gowenlock and coworkers (20, 21, 40) also showed that $CH_2=NOH$, $CH_3CH=NOH$

and $(CH_3)_2C=NOH$ were formed from their corresponding alkyl radicals and NO. These workers estimated activation energies of about 30 to 40 kcal mole^{-1}. On the other hand, Woodall and Gunning (41, 42) investigated the room temperature Hg-sensitized decomposition of C_3H_8 in the presence of NO, and found the oximes $(CH_3)_2C=NOH$ and $C_2H_5CH=NOH$. They believed that the exothermicity of the addition of NO to R brought about the isomerization. There is, of course, also the possibility that the isomerization was aided further by some excess energy of the propyl radicals which they retained from their formation. In the case of i-C_4H_{10}, where $(CH_3)_3C$ is the main radical, they found only $(CH_3)_3CNO$ and no oxime.

In general, one can assume that the isomerization to oximes requires some activation energy. The more labile are the α hydrogen atoms of the nitroso compound, the lower is the activation energy. Nitrosoiso-propane and -butane isomerize at room temperature, whereas nitroso-methane and -ethane require 160°C in the gas phase.

5. Reactions of oximes

Kinetic studies of the pyrolysis of formaldoxime show (43, 44, 45) that at temperatures up to 415° C NO catalyses the decomposition of the oxime giving rise to two different sets of main products, as follows:

$$H_2C{=}NOH \longrightarrow HCN + H_2O$$

$$H_2C{=}NOH \longrightarrow CO + NH_3.$$

Around 500° C autoignition occurs, the main products being nitrogen, carbon monoxide and hydrogen. Under these conditions NO is consumed in larger quantities.

A more detailed study has been made of the decomposition of acetaldoxime (46, 47, 48). As many as 15 products were found, acetonitrile and water being the major ones. Addition of NO strongly accelerated the decomposition of the oximes.

D. Recent Theories of Nitric Oxide Inhibition

There have been several attempts to interpret the inhibition of gas-phase pyrolyses in terms of free-radical mechanisms. The more prominent of these general proposals will be discussed now.

1. The Voevodsky Proposal

Voevodsky (49) suggested that in the pyrolyses of hydrocarbons the chain-propagating steps were homogeneous reactions, but that initiations were irreversible and reversible processes occurring on the surface of the reaction vessel. Nitric oxide or other inhibitors adsorbed on the vessel walls were postulated to suppress the irreversible initiations. Maximum inhibition would correspond to a complete coverage of active centers on the walls. In the gas phase a steady-state concentration of radicals would be maintained by the reversible dissociation and recombination reactions occurring on the surface of the vessel, the rates of these reactions on a chemically inert surface being always the same. This would mean that the amount of inhibitor required for inhibition should be dependent on the surface/volume ratio. It seems that no explanation was envisaged for the acceleration of the decompositions at higher NO concentrations. Recent investigations of n-butane (50), propane (51) and ethane (13, 14, 15) show that a change in surface/volume ratio has little or no effect on the uninhibited decomposition. Also, in the case of the fully-inhibited decompositions of ethane (52) and butane (16), little or no surface effect was observed. It must be admitted, however, that considerable surface effects have been reported for some hydrocarbons. For further details on this controversy the reader may consult Gowenlock's review (24). Recently, Back and Laidler (53) pointed out that for the Voevodsky proposal to apply to the inhibited decomposition of ethane, the surface initiation would have to account for more than 90 % of the whole, and after considering various plausible surface initiations or terminations they concluded that Voevodsky's suggestion did not apply. One unequivocal objection to Voevodsky's theory is that it does not account for consumption of nitric oxide.

2. The Laidler-Wojciechowski Proposal

The Laidler-Wojciechowski proposal, which has been applied to the decompositions of ethane (52, 54), propane (55), butane (56), dimethyl ether (17), diethylether (57), acetaldehyde (58) and propionaldehyde (59), was based on the following ideas. In the presence of NO there is

(i) an additional initiation process, the abstraction of a hydrogen atom from the substrate molecule,

(ii) an additional termination process involving the reaction of a radical with HNO, RNO or the oxime, which arises from RNO. This termination leads to regeneration of NO.

The following mechanism for the pyrolysis of ethane inhibited by NO was proposed (52):

$$C_2H_6 + NO \xrightarrow{1} C_2H_5 + HNO$$

$$C_2H_5 \xrightarrow{2} H + C_2H_4$$

$$H + C_2H_6 \xrightarrow{3} H_2 + C_2H_5$$

$$H + NO \underset{-4}{\overset{4}{\rightleftarrows}} HNO$$

$$C_2H_5 + HNO \xrightarrow{-1} C_2H_6 + NO$$

The steady-state rate derived from this scheme is given by

$$v = k_2 \left[C_2H_5\right] = \left(\frac{k_1\ k_3\ k_{-4}}{k_2\ k_{-1}\ k_4}\right)^{1/2} \left[C_2H_6\right] .$$

Since $\frac{k_1 \quad k_{-4}}{k_{-1} \quad k_4} = \frac{[H]\ [R]}{[RH]} = K_{eq.}$ = a constant,

$$v = \left(\frac{k_3}{k_2}\ K_{eq.}\right)^{1/2} \left[C_2H_6\right] .$$

It will be noticed that the initiation taking place in the absence of NO was omitted and that no provision was made for the formation of methane. The reason for this is that the proposed mechanism was not supposed to apply over the whole range of NO concentrations. It was assumed that at maximum inhibition reaction 1 was so much faster than $C_2H_6 \longrightarrow 2\ CH_3$ that the latter could be neglected. An important feature of the mechanism is that at maximum inhibition the rate is independent of inhibitor concentration and even of the nature of the inhibitor. This means that the mechanism would apply to any inhibitor which is able to function in a way analogous to NO. The mechanism also implies that no consumption of NO takes place at maximum inhibition. This mechanism gave good agreement with the experimental orders and activation energy as derived from pressure measurements.

3. The Norrish-Pratt Proposal

Norrish and Pratt (60) proposed a general mechanism for NO-inhibited paraffin pyrolyses at high temperatures; it had the following main features:

(i) The initiation reactions are the same as in the uninhibited decompositions.

(ii) When inhibition is large the normal termination steps can be neglected and termination takes place via oxime decomposition, the oximes arising from the nitroso-compounds which in turn were thought to arise from the NO scavenging radicals in the system.

(iii) The self-accelerating nature of these pyrolyses was explained by the occurrence of degenerate chain branching arising from a second mode of decomposition of the oximes as previously suggested by Pratt and Purnell (46, 47).

At low NO concentrations these branching processes would not be very important, but would become very significant at high NO concentrations. Another interesting feature of this proposal is that it covers the whole range of NO concentrations; there is thus no need for special treatment of the inhibited, maximally-inhibited and induced regions of the reaction. The authors applied their scheme in a simple form to the data obtained by Blackmore and Hinshelwood (61) for the n-pentane pyrolysis at 540° C. Making a plausible choice of rate constants they obtained quantitative agreement with the experimental results. Later Back and Laidler (53) applied the Norrish-Pratt scheme to the NO-inhibited pyrolysis of ethane as follows:

$$\begin{aligned}
C_2H_6 &\longrightarrow 2\ CH_3\\
CH_3 + C_2H_6 &\longrightarrow CH_4 + C_2H_5\\
C_2H_5 &\longrightarrow H + C_2H_4\\
H + C_2H_6 &\longrightarrow H_2 + C_2H_5\\
C_2H_5 + NO &\longrightarrow C_2H_5NO \longrightarrow CH_3CH{=}NOH\\
CH_3CH{=}NOH &\longrightarrow H + \text{products or } CH_3 + \text{products}\\
CH_3CH{=}NOH &\longrightarrow \text{products.}
\end{aligned}$$

They concluded that the scheme did not properly explain the experimental facts known at the time.

In the pyrolysis of pure ethane the conversion of C_2H_5, a μ radical, into C_2H_4 + H is the slow step, while the reaction of the β radical, H, according to

$$H + C_2H_6 \longrightarrow H_2 + C_2H_5$$

is fast. The essential idea of the Norrish-Pratt scheme is that the participation of oximes allows μ radicals to be converted more rapidly into β radicals than in the absence of nitric oxide. A possible reaction in the case of ethane decomposition is

$$CH_3CH{=}NOH + NO \longrightarrow C_2H_4 + 2\ NO + H.$$

Alternatively the radical may instead be converted into the OH radical, another β radical, by a sequence of reactions to be discussed later. The occurrence of such reactions would explain why addition of enough NO does not reduce the rate to zero at maximal inhibition and why the rate increases at high NO concentrations. On the other hand, for reactions like the acetaldehyde pyrolysis the decomposition of the μ radical, CH_3CO, is fast, while the reaction of the β radical, CH_3, according to

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO$$

is slow (62, 63). Hence, the $\mu \longrightarrow \beta$ transition is not rate limiting, and the Norrish-Pratt mechanism then gives no explanation for an enhancement in rate brought about by nitric oxide. As a matter of fact, in the case of acetaldehyde under certain conditions, there is no reduction in rate, but only a steady increase as nitric oxide is added (64).

The previous theories are deficient in not accounting for all of the results. However, the following features all seem to be helpful in understanding the behavior, and one or more of them is to be found in all of the theories proposed:

1) That NO becomes attached to radicals, the resulting species being less active than the original radical.

2) That oximes formed from μ radicals are more rapidly converted into β radicals than are the free μ radicals.

3) That NO can bring about abstraction reaction.

E. Olefins as Inhibitors of Paraffin Pyrolyses

Apart from nitric oxide, olefins have frequently been used as inhibitors in pyrolyses. Hence, a brief discussion of this subject is in order.

The use of olefins as inhibitors in pyrolyses seems to derive from the work of Stubbs and Hinshelwood (65), who found that for a single pressure of n-pentane at 525° C, nitric oxide and propylene reduced the reaction rate to the same minimum value. Later Hinshelwood and coworkers (66, 67, 68) attempted to show the equivalence of propylene and nitric oxide for other paraffins. These results led to attempts (65, 52, 69) to develop a general mechanism describing the phenomena produced by all inhibitors, implying identical kinetic behavior for the two systems nitric oxide-paraffin and propylene-paraffin. Norrish and Pratt (60), reviewing the experimental evidence, concluded that the equality of limiting rates for the two inhibitors had not been established as exact and general. For further details on this subject the reader is referred to the publications by Norrish and Pratt (60), Quinn (70) and Purnell and Quinn (71). It will suffice to conclude with Purnell and Quinn (71) "that inhibition processes may be very complex and that the operative mechanism may depend not only upon the identity of reactants but also upon the physical conditions. There need be no simple, unique mechanistic interpretation to be sought and the assumption that one exists may only lead back to an impasse comparable with that which developed over the role of molecular processes."

II. Object of the Present Investigation

In view of the many controversies concerning the nitric oxide inhibited pyrolyses it seemed necessary to have a fresh look at this problem. In particular, it was obvious that more chemical evidence was needed. Since the details of the uninhibited ethane pyrolysis had partly been solved (13, 14) or were in the process of being settled (15) when this work was taken up, the NO-inhibited pyrolysis of ethane was chosen as an example. It was decided to search for and measure as many products as possible and in particular to trace the fate of nitric oxide.

Chapter II

EXPERIMENTAL AND RESULTS

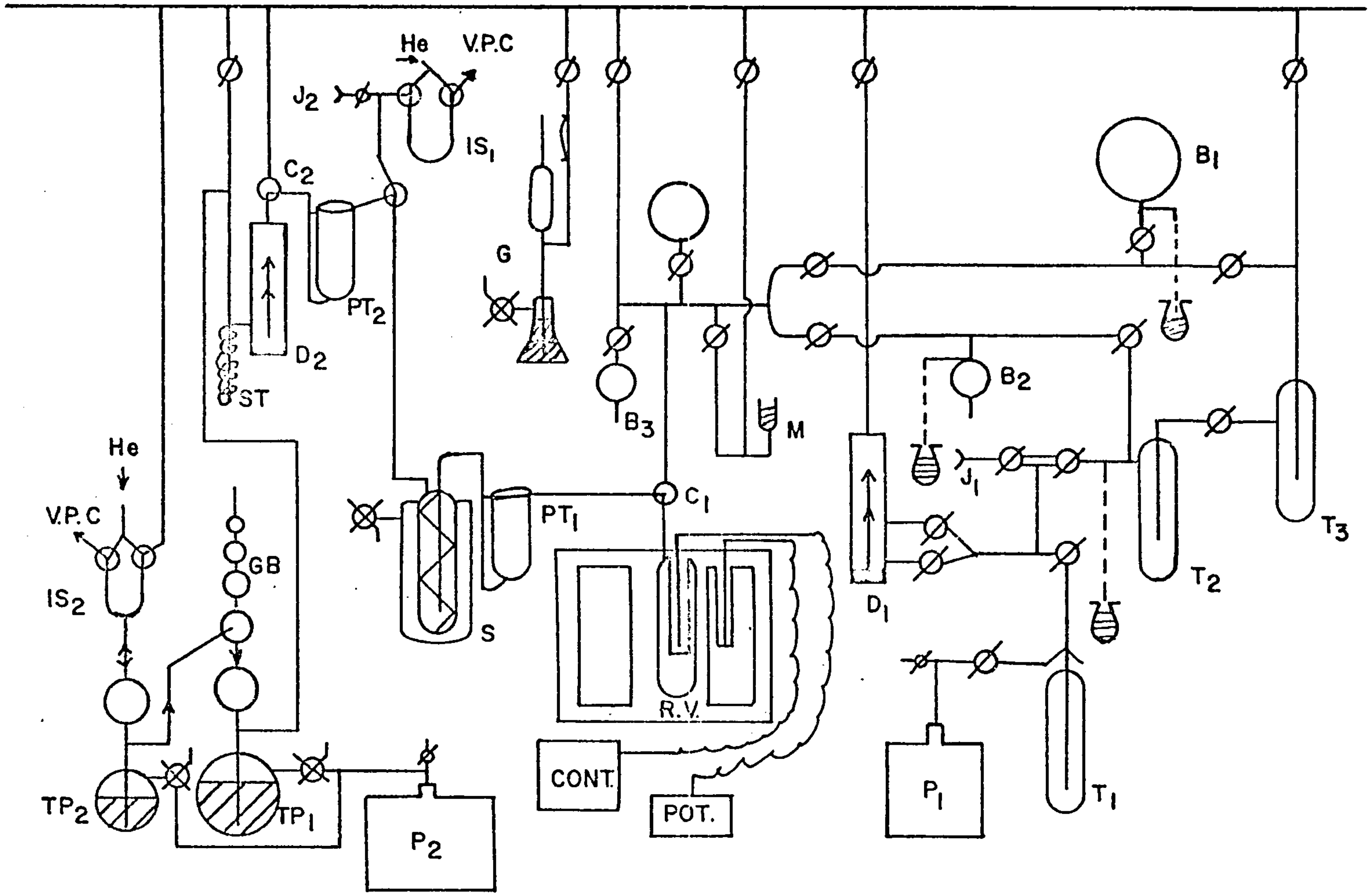
I. Apparatus

The experiments were carried out in a conventional static system, which is shown schematically in Figure 1. All stop-cocks were lubricated with Silicone grease. The entire system could be evacuated to less than 10^{-5} mm Hg by means of an Edwards diffusion pump D_1, which was in series with a liquid nitrogen trap T_1 and a two-stage Welch rotary pump P_1. The residual pressure was measured with a McLeod Gauge G. A single manifold connected all parts of the apparatus. A cylindrical quartz reaction vessel R.V., which had a volume of 344 cc and a surface/volume ratio of 1.0 cm^{-1}, was enclosed in an electrically heated copper cylinder, the walls of which were about 2.5 cm thick. The copper cylinder was well insulated with asbestos.

Temperatures were measured by means of a chromel-alumel thermocouple connected with a potentiometer POT., which was accurate to 0.3° C in the range of temperature studied. The chromel-alumel couple was checked occasionally against a certificated Pt/Pt 13% Rh thermocouple. Absolute temperatures measured

Figure 1

Schematic diagram of the apparatus.



He
V.P.C
J2
IS1
C2
PT2
G
B1
D2
ST
B2
B3
M
J1
He
V.P.C
IS2
GB
PT1
C1
S
T3
T2
D1
R.V.
CONT.
POT.
TP2
TP1
P2
P1
T1

were accurate to ± 1°C. The temperature was controlled with a thermoelectric thermoregulator CONT. The temperature variation during a run was always less than 0.3° C. A temperature gradient along the thermocouple well of the reaction vessel was not detected.

In order to minimize dead space, capillary tubing was used to connect the reaction vessel with stop-cock C_1. The dead space of the reaction vessel was less than 1 % of the volume of the reaction vessel.

The chromatographic system used for the analysis of the products was constructed from components used for the manufacture of the Perkin-Elmer Vapour Fractometer Model 154. The detector was of the thermistor type; it was thermostated in an insulated box by circulating water of constant temperature around the metal block. The columns were immersed in various constant temperature baths. The temperature of both the detector and the columns could be maintained constant within ± 0.1° C. Helium (Linde Company) was used as carrier gas. To remove traces of oxygen and water the gas was first passed through an electrically heated tube filled with copper wool and then through a spiral trap, which was filled with copper shot and immersed in liquid nitrogen. All columns were 1/4 inch in diameter.

II. Experimental Procedure

A. Preparation of Gases

The ethane was a research grade obtained from Phillips Petroleum Company. An appropriate amount of gas was introduced from joint J_1 and condensed into trap T_2 at -196° C. After complete condensation, the stop-cock attached to J_1 was closed, and the liquid nitrogen bath in T_2 was replaced by an isopentane slush at -160° C. Then trap T_3 was immersed in liquid nitrogen and the series of traps was subject to evacuation. Only the middle fraction of ethane was collected. By this procedure traces of air and methane were removed by evacuation and traces of higher hydrocarbons remained in trap T_2. Thus the only impurity detectable by gas-chromatography was a trace of ethylene. An upper limit of this impurity was estimated to be 0.004 %. After distillation the purified ethane was stored in bulb B_1.

Nitric oxide (Matheson Co.) was purified by passing the gas at -80° C through a trap filled with silica gel. The silica gel trap was connected to joint J_1. After passing through this trap the gas was condensed at -196° C in trap T_2. Then the stop-cock attached to J_1 was closed, and the nitric oxide was thoroughly degassed. Finally the liquid nitrogen bath in T_2 was replaced by a liquid oxygen bath and the gas was distilled into the storage bulb B_2, where it was condensed at -196° C. No impurities could be detected by gas-chromatography.

B. Procedure for Experiments

Mixtures of ethane and nitric oxide were prepared by condensing an appropriate amount of ethane in mixing bulb B_3. The ethane was briefly degassed and then allowed to warm up to room temperature, after which a pressure reading was taken with manometer M. After condensing again the ethane, an appropriate amount of degassed nitric oxide was added to B_3. Then the liquid nitrogen bath was removed from B_3 and both gases were permitted to warm up to room temperature. From the pressure change the percentage composition of the mixture could be calculated. Changes in the ambient temperature were taken into consideration. The reagents were usually allowed to mix over-night by diffusion. When the nitric oxide had been stored for a longer period of time it was again distilled - as described above - before use. The quantity of mixture prepared was sufficient to make a series of runs.

Before each experiment the system was evacuated to a pressure lower than 10^{-5} mm. The initial pressure of the reactants was measured with manometer M. At the end of an experiment the products and reactants were removed through a series of traps, which were, in order: a solid nitrogen trap PT_1, a Le Roy still S, a solid nitrogen trap PT_2, followed by a Toepler pump TP_1 and a gas burette GB. A mercury diffusion pump D_2 between the trap PT_2 and the pump TP_1 aided collection of the noncondensible gases. When the noncondensible gases had been collected in the gas burette, PT_1 was warmed to room temperature and the Le Roy still S to -162° C. Traces of occluded noncondensible gases were then collected while the ethane and nitric oxide distilled into the trap PT_2. After completion of the distillation the Le Roy still was warmed to about 40° C and the condensibles were collected in a U-tube IS_1 immersed in liquid nitrogen.

For each series of runs, where the noncondensibles were measured, a nitrogen blank was determined to correct the nitrogen yield for a trace of nitrogen in the reactants and for small amounts of air leaking into the system while collecting the noncondensibles. This correction was usually less than 1 % of the total nitrogen yield at moderate conversions. Only at very low conversions of mixtures containing low concentrations of nitric oxide was this correction significantly larger.

C. Analyses of Products

In most experiments the conversion of ethane was kept between .5 and 3 %. In some experiments conversions were as low as 0.1 % or as high as 10 %. The conversion of NO varied between 0.2 and 15 %.

Calibration of detector:

The detector of the chromatographic system was calibrated for all products except water by injecting known amounts of products which were measured in the gas burette GB. The capillary and the three smallest bulbs of the burette were calibrated by filling them with mercury. These calibrations were accurate to within 0.1 %. In most cases the measurements of the products with the gas burette were in error by not more than 1 %. The reproducibility of the calibrations as such was not better than ± 2 %. Calculations were based on the ideal gas law except for acetonitrile, where a small correction for nonideality was applied by means of the second virial coefficient (72).

For water the calibration procedure was different. Mixtures of acetonitrile and water with varying amounts of water were made up and the accurate number of micromoles of water per microlitre of solution was determined by the Karl Fischer method (73). Then a certain amount of solution was injected through a rubber septum into a slow stream of dry helium by means of a microlitre syringe. The vapours were then trapped out in a spiral trap which contained some glass beads and which was immersed in liquid nitrogen. After injection and trapping were completed the spiral trap, which could be closed by stop-cocks, was connected to joint J_2. Then the helium was pumped off and the vapours were collected at -196°C in IS_1, from which they could be injected into the chromatographic system. Small corrections had to be made for "bleeding" of the syringe needle which amounted to no more than 5 % of the total value. The reproducibility of the calibrations was about ± 5 %.

In order to correct for slight variations in retention times, calibrations were made as functions of retention times over the range of variations normally encountered. The calibrations of all products were frequently checked.

The analytical problems of this work required an extensive search for suitable chromatographic columns during the course of which the products were identified on at least two different columns by their retention times.

In some cases identification was made on as many as five columns.

Noncondensibles:

Noncondensibles were collected in the gas burette GB as described previously. After collection was completed the products were transferred by means of the Toepler pump TP_2 and the Welch rotary pump P_2 into the injection U-tube IS_2. They were then analysed gas-chromatographically on a 3 m silica gel column (60/80 mesh) by sweeping the sample from IS_2 with helium. The column temperature was -35° C. To obtain a good resolution of all products the silica gel was heated (74) for several hours at 600° C and the column temperature had to be low. The order of elution was H_2, N_2, NO, CO, CH_4. Nitric oxide was, of course, not a product, but small amounts of this reactant occasionally escaped from the trap PT_2. Larger amounts of NO interfered with the measurement of CO. This was not serious, however, because CO was a minor secondary product and was only measured rarely. The primary products H_2, N_2 and CH_4 could always be measured without any interference. For hydrogen peak heights were measured, for nitrogen and methane peak areas.

Ethylene and Nitrous Oxide:

Nitrous oxide and ethylene cannot be separated from ethane by distillation and hence a column had to be found which can separate the large excess of reactants from these two products. After an extensive search a 4 m long column filled with activated alumina (Burell, No. 341-35) was found to give acceptable results. The order of elution was NO, C_2H_6, N_2O, C_2H_4 with a column temperature of $-35^\circ C$. For runs where the ethane pressures were higher than 150 mm the resolution of the ethane and nitrous oxide peaks became unacceptable, but ethane and ethylene could still be separated up to almost 300 mm pressure of ethane. The nitrous oxide peak was on the tail end of the ethane peak; this, however, did not introduce any serious error, because calibrations were performed under identical conditions. Because of the analytical requirements, separate runs had to be made for the analysis of nitrous oxide and ethylene. After condensing the products and excess reactants in trap PT_1 and pumping off the non-condensibles - which were discarded - the trap PT_1 was warmed to room temperature. The products were condensed in S and after warming S to $-135^\circ C$, C_2H_4, NO, C_2H_6 and N_2O were distilled and condensed into IS_1. From IS_1 the sample was injected into the chromatographic system. For nitrous oxide and ethylene, peak areas were measured.

Water and Acetonitrile:

For convenience separate runs were made for the determination of water and acetonitrile. After trapping out the products and excess reactants in PT_1 and pumping off the noncondensibles, PT_1 was warmed to room temperature, and the gases were condensed in S. Then the temperature in S was adjusted to -160° C and all volatile gases were pumped off and discarded. Water, acetonitrile and other condensibles - which will be discussed below - remained in S. After completion of the distillation, S was warmed to 40° C and the products were collected at -196° C in IS_1. Then they were analysed on a 1 m Chromosorb T (40/60 mesh) column coated with 20 % Carbowax 400. The column temperature was 72° C. The order of elution was CH_3CN, H_2O, the water peak showing some tailing. The other products present did not interfere with the analysis of these two compounds. Because of the "stickiness" of water and acetonitrile on the glass and grease, the collection of these products in trap IS_1 took about two hours. It was also found advantageous to add helium to the products condensed in IS_1 and then to immerse IS_1 in hot water before injecting them into the column. For acetonitrile peak heights were measured, for water peak areas, using a planimeter.

Other condensible products:

The following secondary products were detected in small amounts: n-butane, butene-1, cis- and trans-butene-2, butadiene-1,3, hydrogen cyanide and acetaldehyde. These products were measured occasionally in separate runs. The procedure was the same as for water and acetonitrile. No loss of products due to distillation could be detected under the experimental procedures employed. The hydrocarbon products were analysed on a 15 ft. Chromosorb P (60/80 mesh) column coated with 15 % Dimethylsulfolane. The order of elution was C_4H_{10}, C_4H_8-1, trans- and cis-C_4H_8-2, C_4H_6. The column was kept at 0° C. The other condensibles did not interfere with the analysis.

Hydrogen cyanide and acetaldehyde were analysed on a 2 m Porapak Q column (80/100 mesh) with a column temperature of 72° C. The hydrogen cyanide appeared on the tail end of the water peak, but no serious difficulty was encountered in the separation. Other products did not interfere with the analysis.

Consumption of NO:

Some runs were made at lower NO concentrations, where the disappearance of NO was directly measured. The procedure was as follows: The reactants were admitted to R. V. and immediately removed into trap PT_1 in order to keep the conversion negligible. Traces of noncondensible products were pumped off. Then PT_1 was warmed to room temperature and the reactants were collected in S. Then S was warmed to -160° C and both reactants were distilled into trap PT_2 which was kept at -196° C. The vapour pressure of NO is high enough for it to distill - aided by D_2 - from PT_2 into the spiral trap ST, which was kept at -196° C. When most of the NO had distilled into ST, stop-cock C_2 was closed, the liquid nitrogen bath removed and the gas was toeplered into the gas burette GB. Then C_2 was opened again and the remaining NO was collected. Since also some C_2H_6 was distilled, a small correction had to be made for this. The amount of NO calculated using the ideal gas law was then equal to the initial concentration of NO. The method could be checked by using this value of NO to compute the composition of the mixture. Calculations showed that the percentage composition derived in this way agreed within ± 1 % with that determined previously. For the actual runs the same procedure was employed and hence the remaining NO concentration determined. Although the nitric oxide concentrations can be determined accurately, the nitric oxide consumption is possibly affected with an error of 10-15 %, because it is obtained as the small difference of two large numbers.

Products not detected:

A search was made for the presence of methylnitrite, ethylnitrite, nitromethane, nitroethane, methylnitrate, ethylnitrate, methylalcohol, ethylalcohol, dimethylether, diethylether, formaldehyde and ammonia. None of these could be found.

III. Results

A. The Products of the Reaction

Comprehensive analytical studies showed that the only products at the initial stage of decomposition were ethylene, hydrogen, water, nitrogen, nitrous oxide, methane and acetonitrile. The relative yields of all products were dependent on the composition of the C_2H_6-NO mixture. At very low NO concentrations, ethylene and hydrogen were the main products. As the NO concentrations were increased, water became a main product instead of hydrogen. The yields of acetonitrile were always much smaller than those of all other products.

As the reaction time increased, carbon monoxide, hydrogen cyanide, acetaldehyde, butane, butene-1, butadiene-1,3 and cis- and trans-butene-2 were also detected and occasionally measured.

B. Decomposition of pure Ethane

In order to check the experimental procedure and to obtain information about the formation of ethylene, hydrogen, methane and butane in the absence of NO under the experimental conditions of this work, a series of runs was made with pure ethane at 596° C. The initial rates are shown in Table 1 and the order plots in Figure 2.

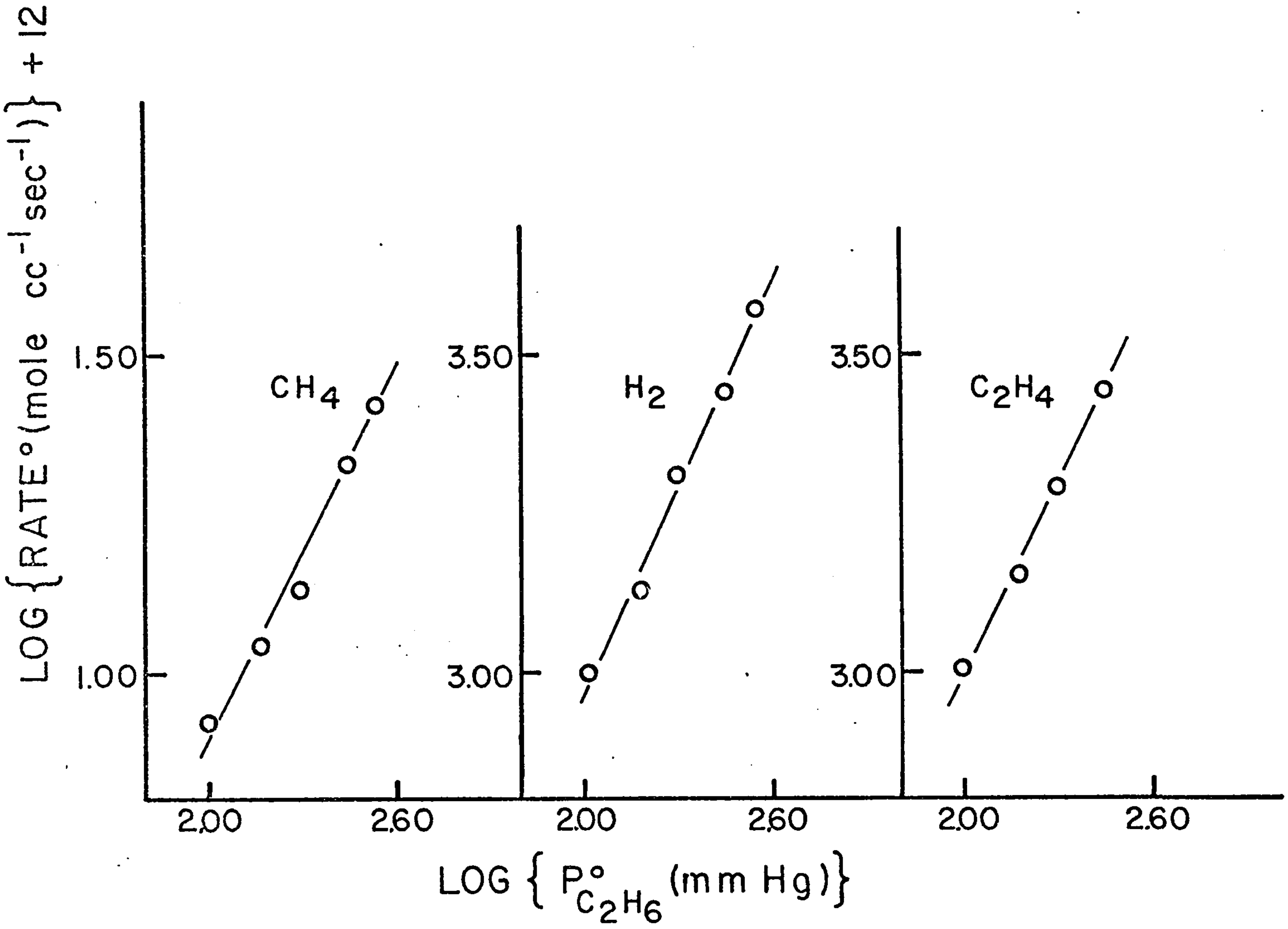
Table 1

Initial rates of production of hydrogen, ethylene, methane and butane as functions of ethane pressure. Data were obtained at 596° C in the absence of nitric oxide.

$P^o_{C_2H_6}$ mm Hg	$v^o_{H_2} \times 10^9$ $\frac{\text{mole}}{\text{cc sec}}$	$v^o_{C_2H_4} \times 10^9$ $\frac{\text{mole}}{\text{cc sec}}$	$v^o_{CH_4} \times 10^{11}$ $\frac{\text{mole}}{\text{cc sec}}$	$v^o_{C_4H_{10}} \times 10^{11}$ $\frac{\text{mole}}{\text{cc sec}}$
346.0	3.72	-	2.62	-
273.3	2.75	2.76	2.12	-
193.5	2.03	1.96	1.37	-
148.5	1.33	1.42	1.10	-
100.0	1.00	1.01	0.843	0.237

Figure 2

Order plots for the production of methane, hydrogen and ethylene at 596° C in the absence of nitric oxide.


LOG {RATE°(mole cc^{-1}sec^{-1})} + 12
1.50
1.00
3.50
3.00
3.50
3.00
CH$_4$
H$_2$
C$_2$H$_4$
2.00
2.60
2.00
2.60
2.00
2.60
LOG {P°$_{C_2H_6}$(mm Hg)}

One observes that the rates of hydrogen and ethylene are equal as found previously (13). The orders of methane, hydrogen and ethylene productions are 1.00, 1.05 and 1.00 respectively. This is in good agreement with the results of other workers (13, 14, 15).

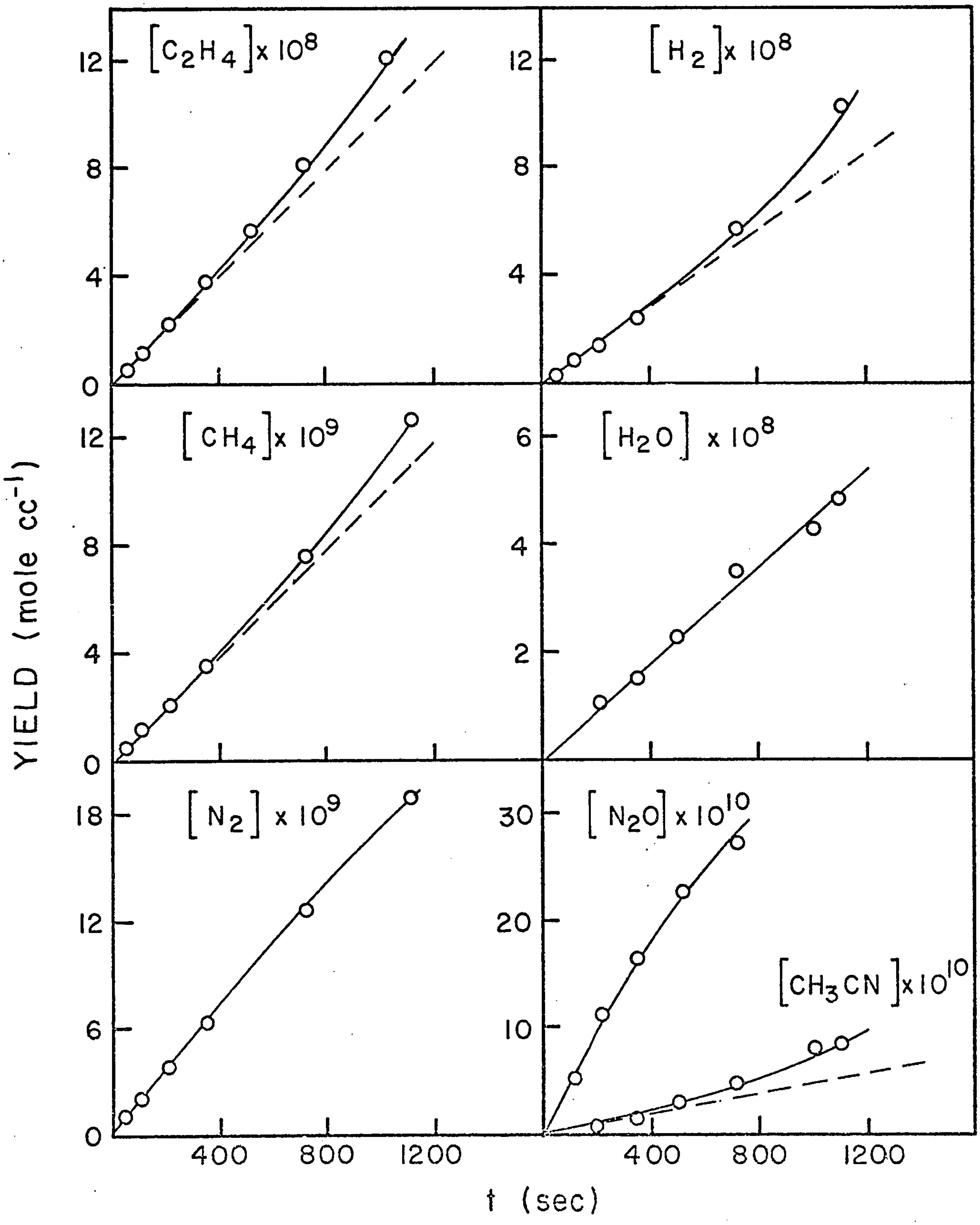
C. The Production of Hydrogen

Typical hydrogen production plots are shown in Figures 3 and 4, in which conversions went up to 7 % for ethane and 15 % for nitric oxide and 9 % for ethane and 6.5 % for nitric oxide, respectively. The rate of production increased from a finite initial value as the reaction progressed.

The initial rate $v^o_{H_2}$ was obtained by extrapolating the $[H_2]/t$ vs. time plot to zero contact time. Typical examples of this procedure are given in Figures 5 and 6. In many cases the rate of change of rate with time was small, and when this was so the rates derived from individual runs at low conversions were averaged and taken to be initial rates. Double logarithmic plots of $v^o_{H_2}$ vs. $P^o_{C_2H_6}$ and $v^o_{H_2}$ vs. P^o_{NO} are shown in Figures 7 and 8 respectively. The order with respect to ethane is constant within experimental error at pressures between 100 and 346 mm Hg at 596° C. The order with respect to nitric oxide changes from a negative value at low NO

Figure 3

Yield-time plots for ethylene, hydrogen, methane, water, nitrogen, nitrous oxide and acetonitrile production at 596° C. Results were obtained from a mixture containing 100.0 mm C_2H_6 and 18.6 mm NO. Highest conversion is 7 % for C_2H_6 and 15 % for NO.



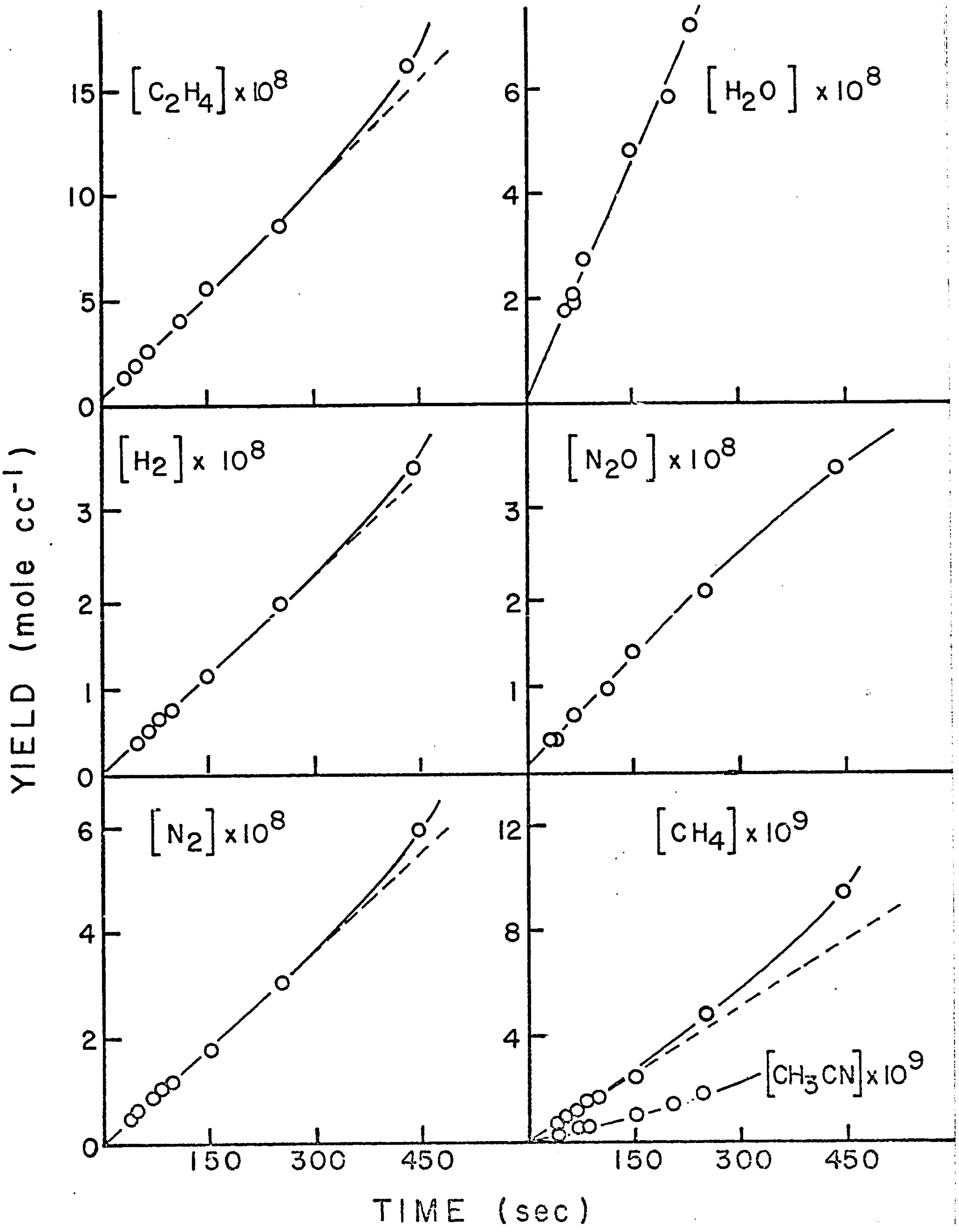
[C$_2$H$_4$] x 10^8
[H$_2$] x 10^8
[CH$_4$] x 10^9
[H$_2$O] x 10^8
[N$_2$] x 10^9
[N$_2$O] x 10^{10}
[CH$_3$CN] x 10^{10}
YIELD (mole cc^{-1})
t (sec)
0
4
8
12
2
6
18
10
20
30
400
800
1200

Figure 4

Yield-time plots for ethylene, hydrogen, methane, water, nitrogen, nitrous oxide and acetonitrile production at 596° C.

Results were obtained from a mixture containing 100.0 mm C_2H_6 and 162 mm NO.

Highest conversion is 9 % for C_2H_6 and 6.5 % for NO.



[C₂H₄] x 10⁸
[H₂O] x 10⁸
[H₂] x 10⁸
[N₂O] x 10⁸
[N₂] x 10⁸
[CH₄] x 10⁹
[CH₃CN] x 10⁹
YIELD (mole cc⁻¹)
TIME (sec)
0
5
10
15
2
4
6
1
2
3
12
8
150
300
450

Figure 5

Typical rate-time plots for the production of hydrogen.

Data were obtained at 596° C for 83.3 mm NO and varying pressures of C_2H_6.

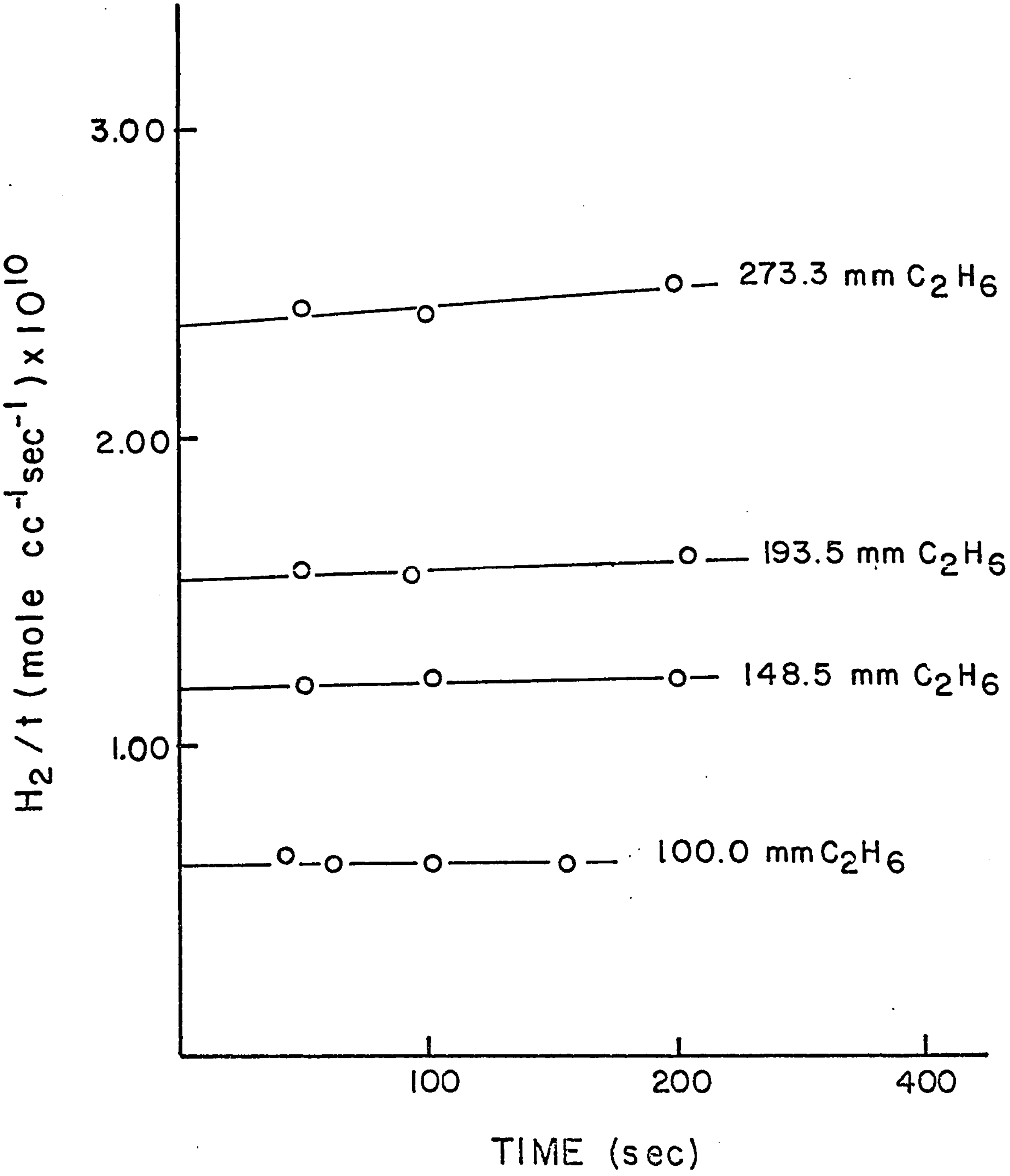

3.00
2.00
1.00
H_2/t (mole $cc^{-1}sec^{-1}$) x 10^{10}
273.3 mm C_2H_6
193.5 mm C_2H_6
148.5 mm C_2H_6
100.0 mmC_2H_6
100
200
400
TIME (sec)

Figure 6

Typical rate-time plots for the production of hydrogen.

Data were obtained for 83.3 mm NO and 100.0 mm C_2H_6 and temperatures of 549.9° C, 564.8° C and 580.7° C.

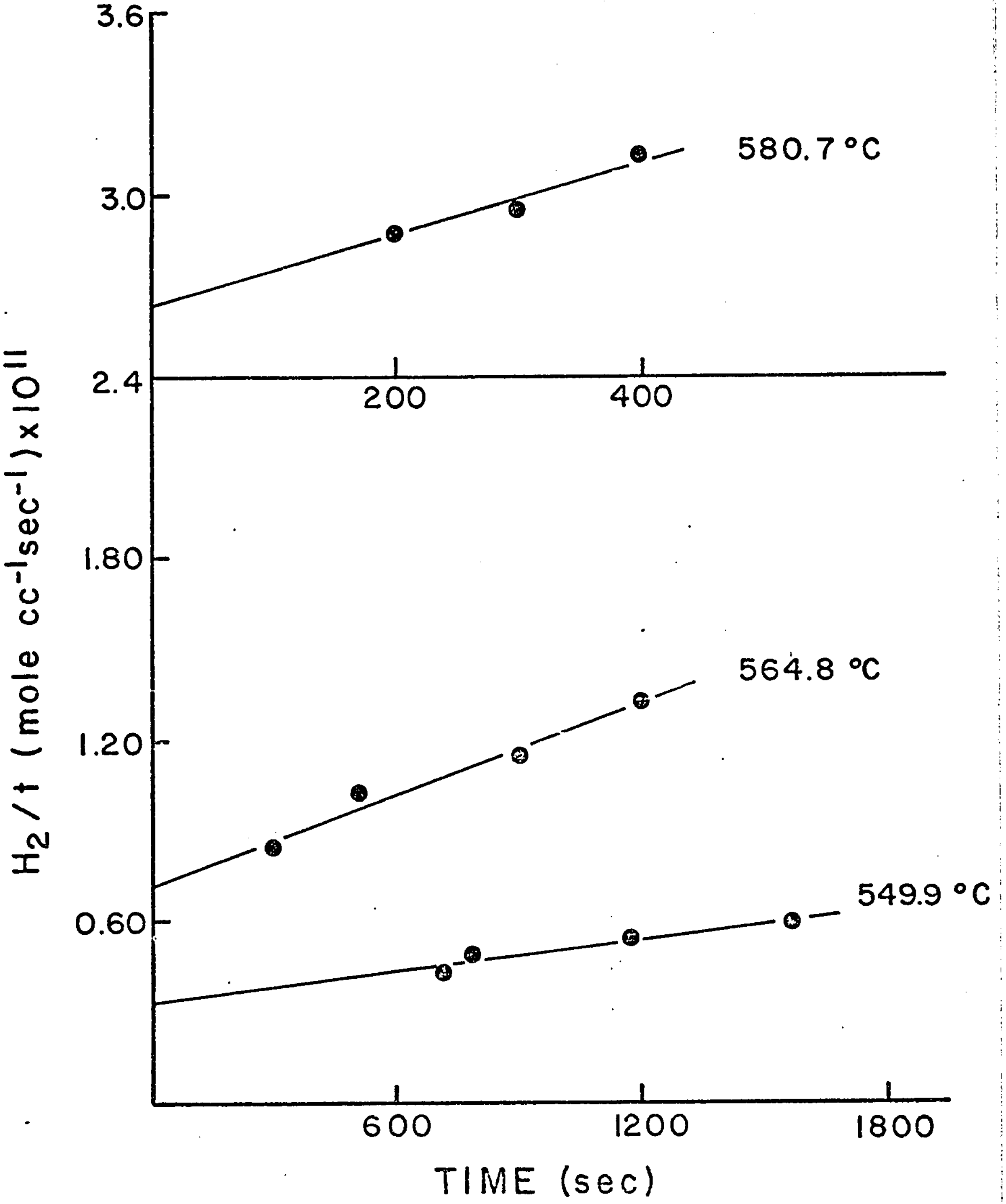

3.6
3.0
2.4
1.80
1.20
0.60
200
400
600
1200
1800
580.7 °C
564.8 °C
549.9 °C
H_2/t (mole cc^{-1}sec^{-1}) x 10^{11}
TIME (sec)

Figure 7

Order plots for the production of ethylene, water, hydrogen, nitrogen, nitrous oxide, methane and acetonitrile at 596° C.

Data were obtained with 83.3 mm NO and varying pressures of C_2H_6.

Δ CH_4 refers to the rate of CH_4 minus that in the absence of NO.

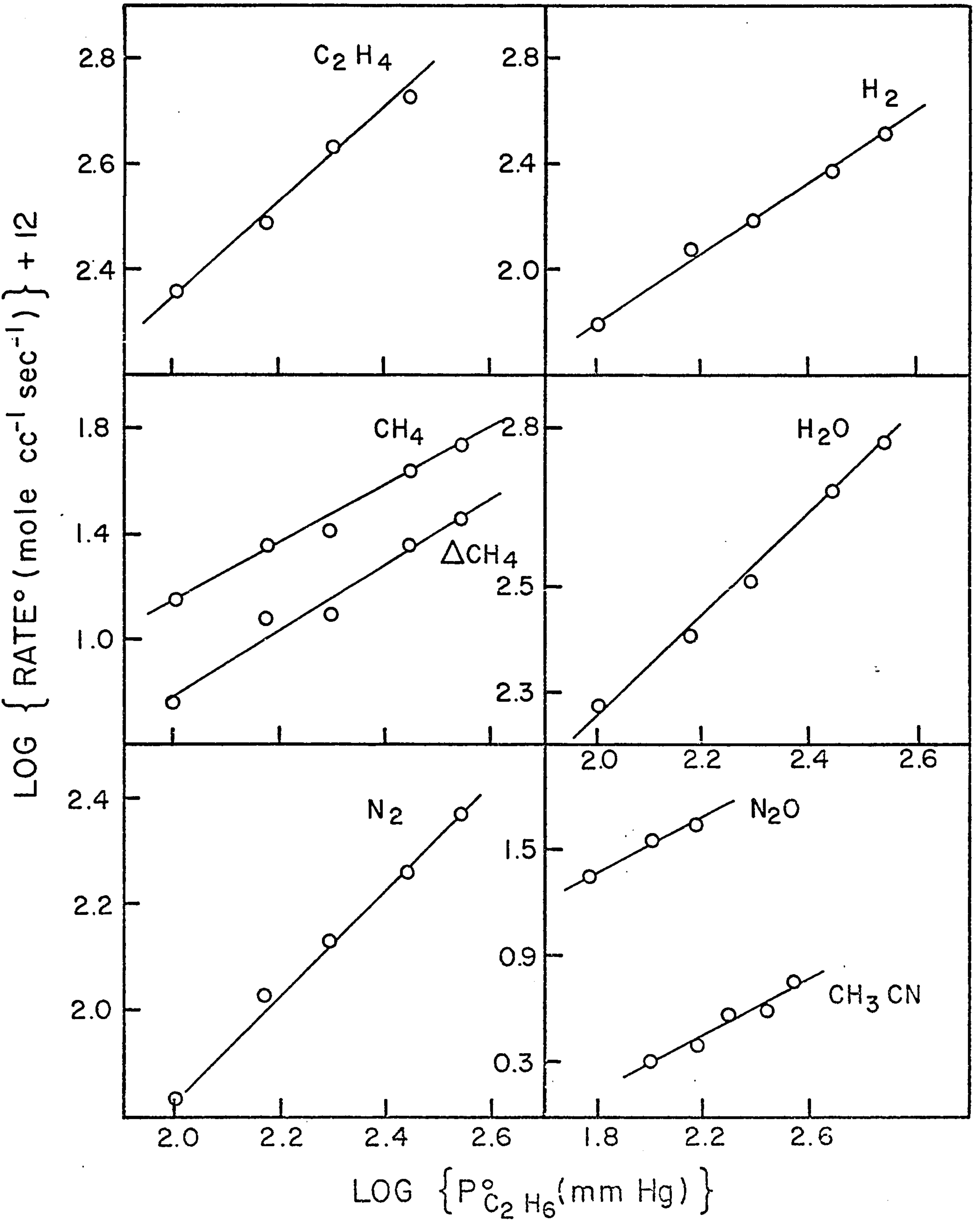
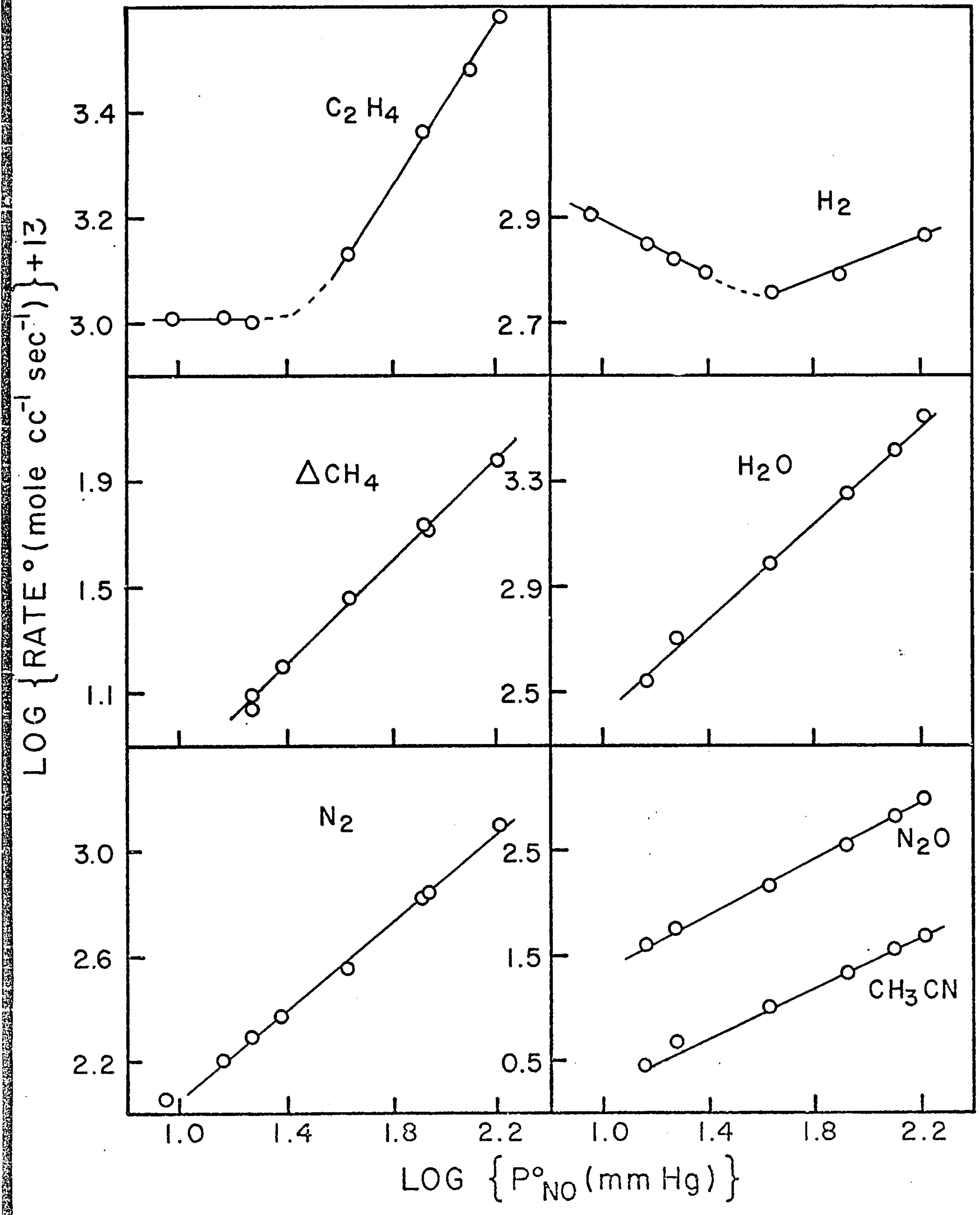

LOG {RATE° (mole cc⁻¹ sec⁻¹)} + 12
LOG {P°C2H6 (mm Hg)}
C2H4
2.8
2.6
2.4
H2
2.8
2.4
2.0
CH4
ΔCH4
1.8
1.4
1.0
H2O
2.8
2.5
2.3
2.0
2.2
2.4
2.6
N2
2.4
2.2
2.0
N2O
CH3CN
1.5
0.9
0.3
2.0
2.2
2.4
2.6
1.8
2.2
2.6

Figure 8

Order plots for the production of ethylene, water hydrogen, nitrogen, nitrous oxide, methane and acetonitrile at 596° C.

Data were obtained with 100.0 mm C_2H_6 and varying pressures of NO.

ΔCH_4 refers to the rate of CH_4 minus that in the absence of NO.


LOG {RATE° (mole cc⁻¹ sec⁻¹)} + 12
LOG {P°NO (mm Hg)}
C2 H4
H2
ΔCH4
H2O
N2
N2O
CH3 CN
3.4
3.2
3.0
2.9
2.7
1.9
1.5
1.1
3.3
2.9
2.5
3.0
2.6
2.2
2.5
1.5
0.5
1.0
1.4
1.8
2.2
1.0
1.4
1.8
2.2

pressures to a positive value at high NO pressures. It is zero around 43 mm NO, corresponding to a composition of 30 % NO.

Figure 9 gives two Arrhenius plots. Least-squares treatment of the data leads to activation energies of 106 kcal mole^{-1} for the mixture consisting of 18.6 mm NO and 100.0 mm C_2H_6 and 95 kcal mole^{-1} for the mixture consisting of 83.3 mm NO and 100.0 mm C_2H_6. Mixtures with the same composition were also used for the determination of the activation energies of the rates of production of the other products. For convenience these mixtures will be referred to as the 15.7 % and the 45.5 % mixtures, respectively.

D. <u>The Production of Ethylene</u>

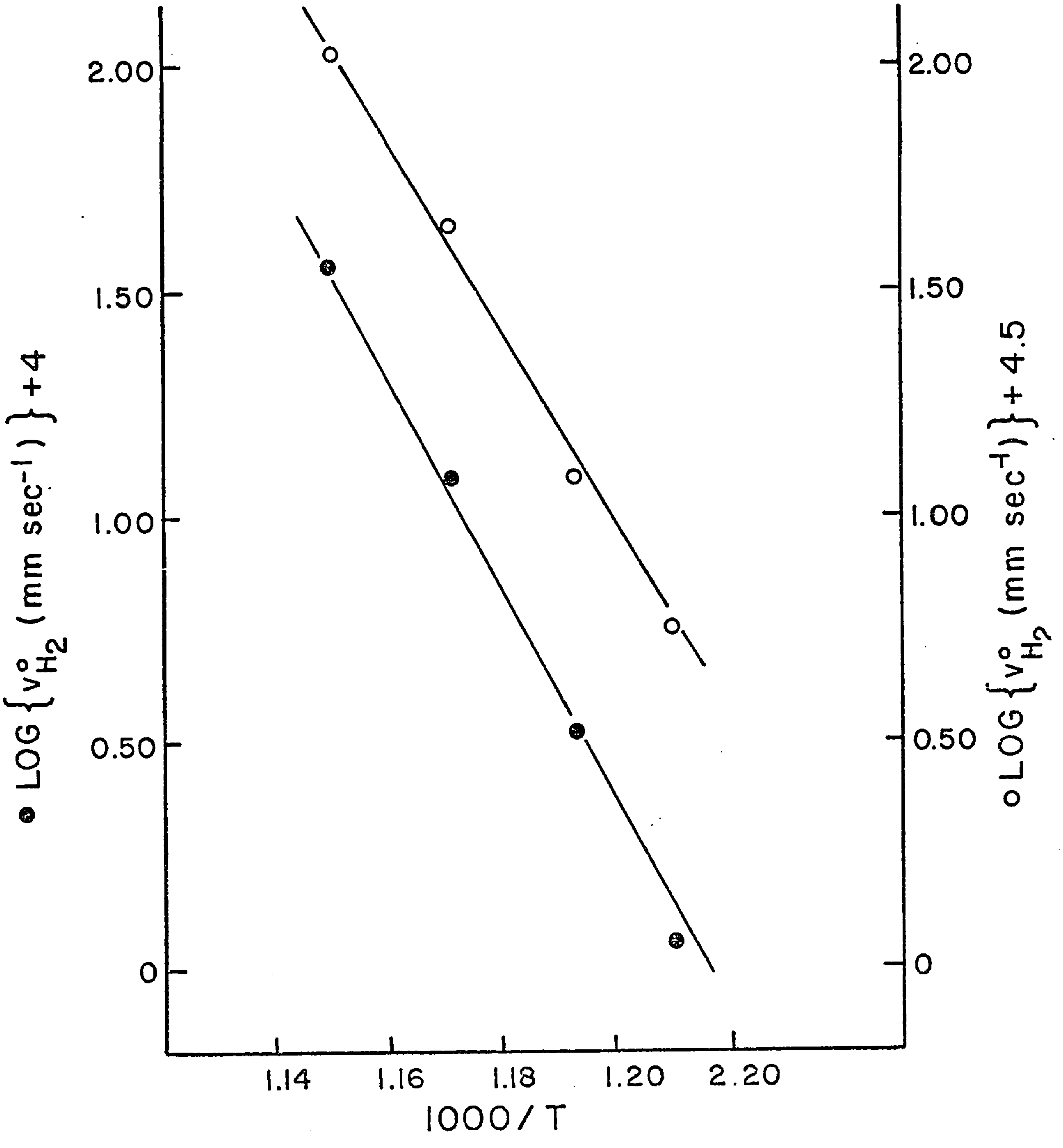
Typical ethylene production plots are shown in Figures 3 and 4. The rate of production increased from a finite initial value as the reaction progressed. Initial rates were obtained by extrapolating the $[C_2H_4]/t$ vs. time plots to zero contact time. Examples of this procedure are given in Figure 10. In most cases, however, rates derived from runs at low conversions were indistinguishable from extrapolated values and in such cases the extrapolation was not made. Double logarithmic plots of $v^o_{C_2H_4}$ vs. $P^o_{C_2H_4}$ and P^o_{NO} are shown in Figures 7 and 8,

Figure 9

Arrhenius plots for hydrogen production

● 15.7 % mixture

o 45.5 % mixture

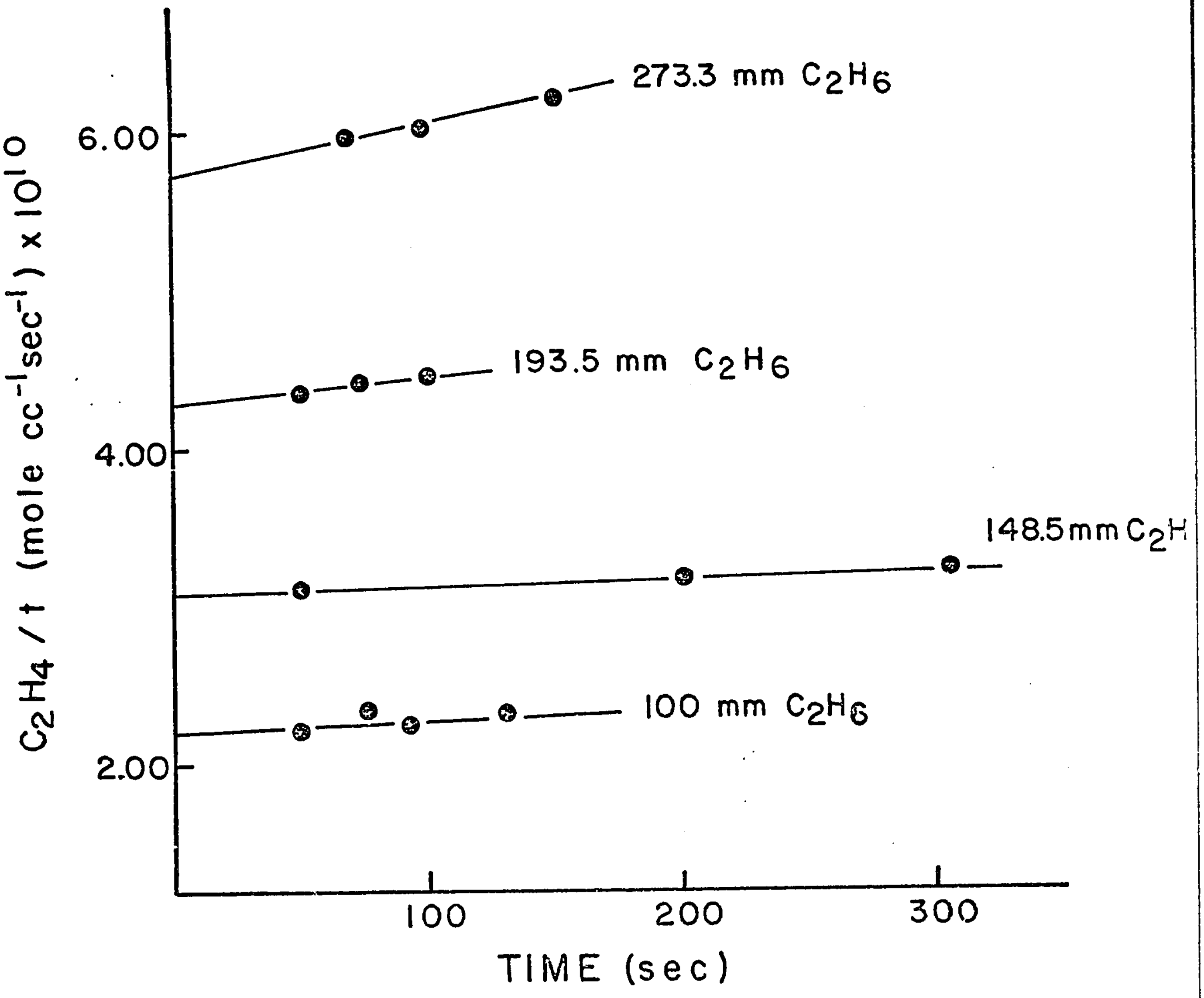


● LOG {$v^{\circ}_{H_2}$ (mm sec^{-1})} + 4
2.00
1.50
1.00
0.50
0
○ LOG {$v^{\circ}_{H_2}$ (mm sec^{-1})} + 4.5
2.00
1.50
1.00
0.50
0
1.14
1.16
1.18
1.20
2.20
1000/T

Figure 10

Typical rate-time plots for the production of ethylene at 596° C.

Data were obtained for 83.3 mm NO and varying pressures of C_2H_6.



273.3 mm C_2H_6
193.5 mm C_2H_6
148.5 mm C_2H
100 mm C_2H_6
6.00
4.00
2.00
100
200
300
TIME (sec)
C_2H_4 / t (mole $cc^{-1} sec^{-1}$) x 10^{10}

respectively. The order with respect to ethane is constant within experimental error at pressures between 100 and 273 mm Hg at 596° C. The order with respect to nitric oxide is zero between 9 and 25 mm NO and it has a constant positive value for greater nitric oxide pressures.

Figure 11 shows two Arrhenius plots. Least-squares treatment of the data leads to activation energies of 66 kcal $mole^{-1}$ and 59 kcal $mole^{-1}$ for the 15.7 % and the 45.5 % mixtures, respectively.

E. The Production of Nitrous Oxide and Acetonitrile

Examples of nitrous oxide and acetonitrile production plots are given in Figures 3 and 4. The rate of production of acetonitrile increased strongly from a finite initial value as the reaction proceeded, whereas that of nitrous oxide decreased. Initial rates were always obtained by the extrapolation procedure described above; typical examples are shown in Figures 12 and 13. Order plots for these two products are shown in Figures 7 and 8. The orders with respect to ethane and nitric oxide were constant within experimental error at all pressures for both products.

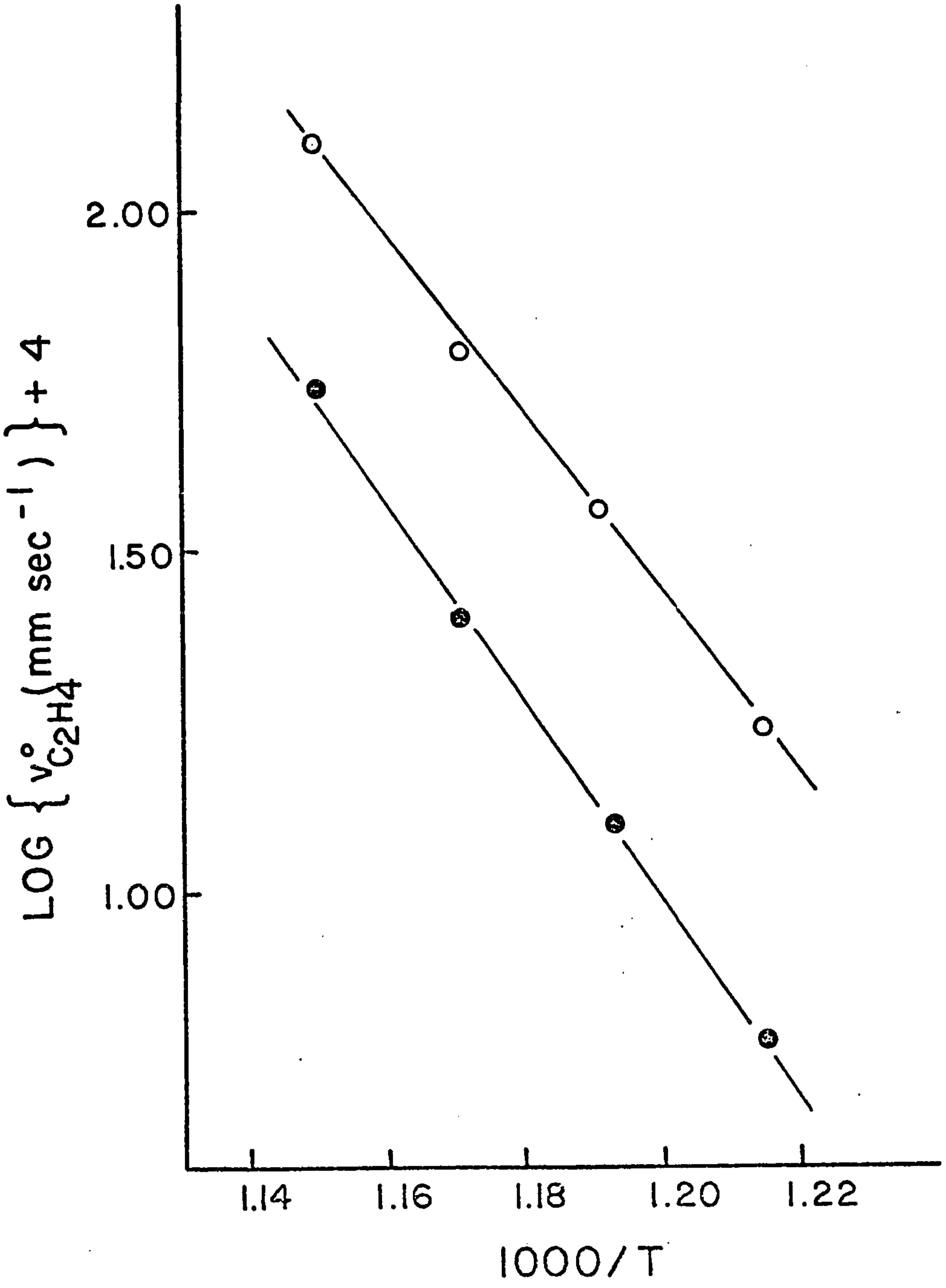
Arrhenius plots for nitrous oxide and acetonitrile are given in Figures 14 and 15, respectively. For the 15.7 % mixture the activation energy for the rate of

Figure 11

Arrhenius plots for ethylene production

● 15.7 % mixture

o 45.5 % mixture



LOG {v°C2H4 (mm sec-1)} + 4
2.00
1.50
1.00
1.14
1.16
1.18
1.20
1.22
1000/T

Figure 12

Typical rate-time plots for the production of acetonitrile.

Data were obtained for 100.0 mm C_2H_6 and varying pressures of NO at 596° C.

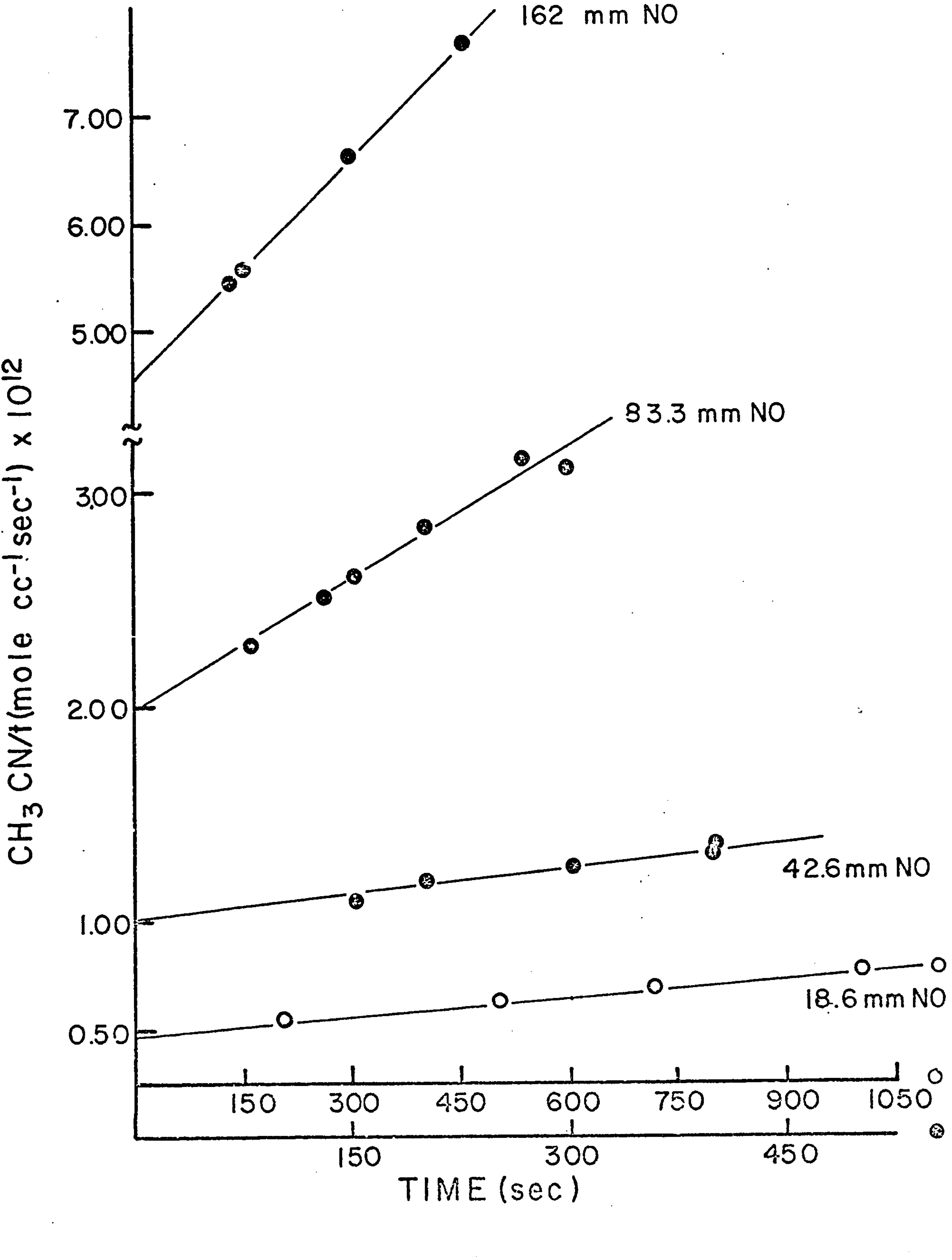
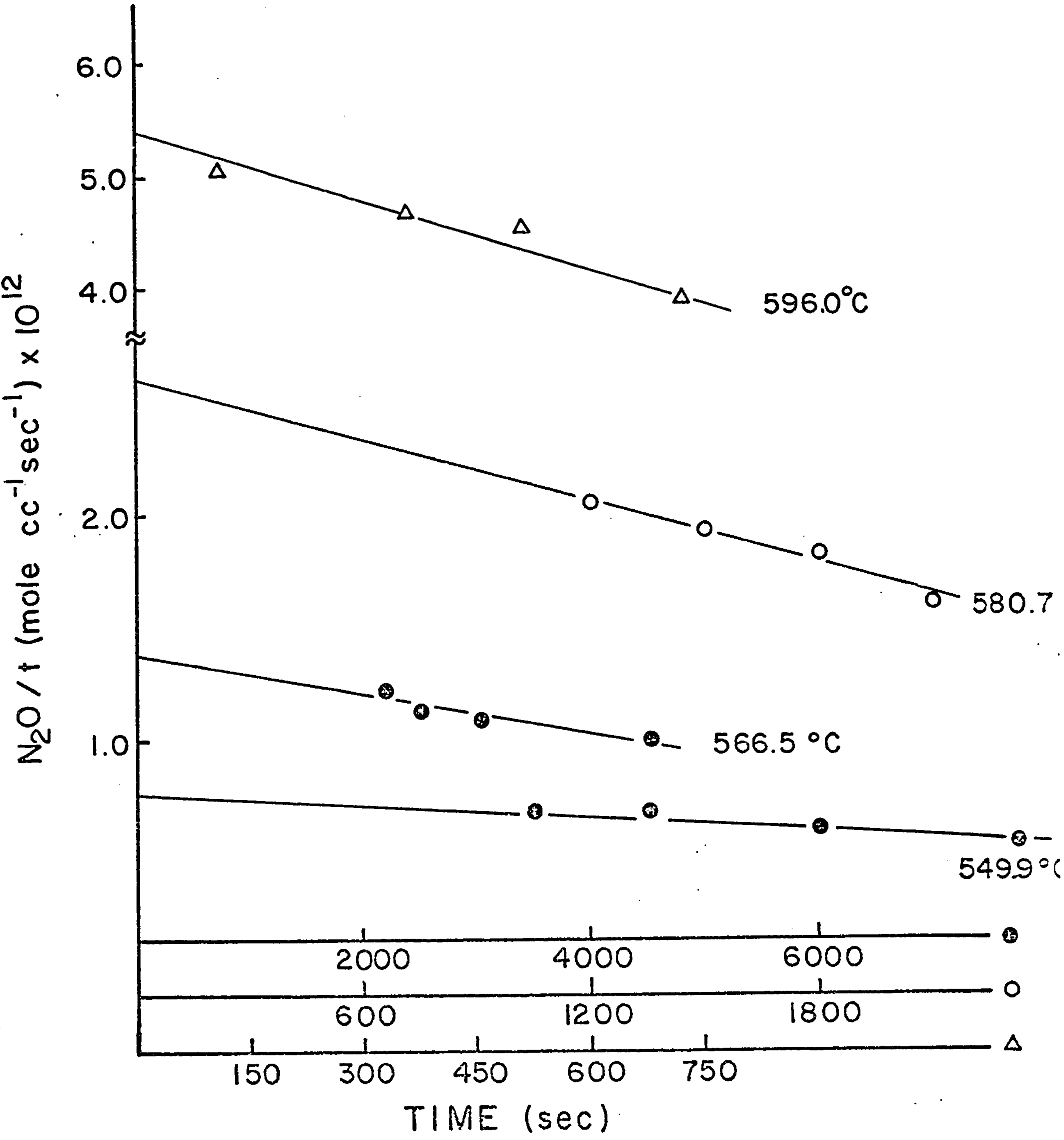

162 mm NO
83.3 mm NO
42.6 mm NO
18.6 mm NO
7.00
6.00
5.00
3.00
2.00
1.00
0.50
CH_3CN/t (mole cc^{-1} sec^{-1}) x 10^{12}
150
300
450
600
750
900
1050
150
300
450
TIME (sec)

Figure 13

Typical rate-time plots for the production of nitrous oxide.

Data were obtained for 18.6 mm NO and 100.0 mm C_2H_6 at varying temperatures.



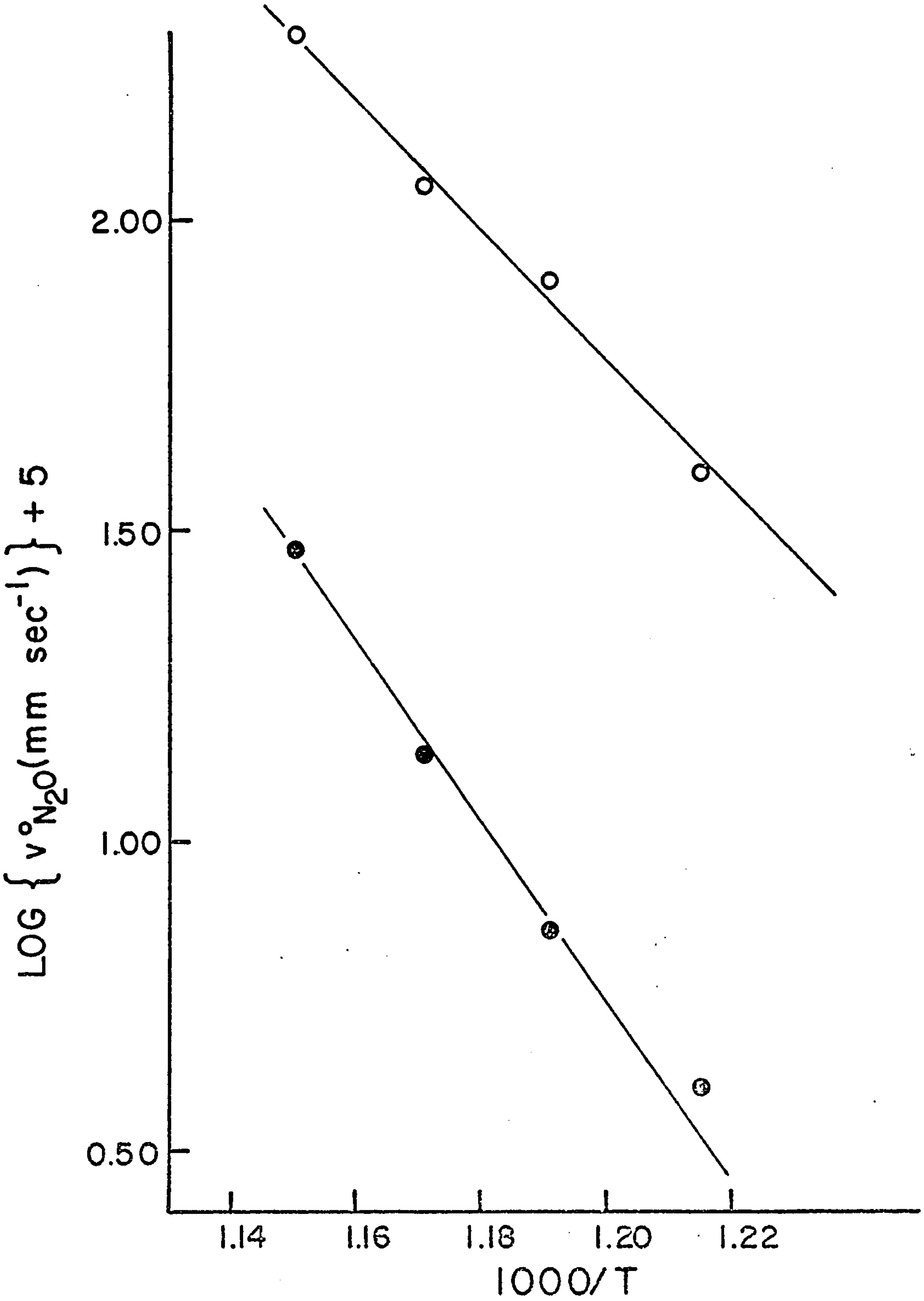
6.0
5.0
4.0
2.0
1.0
N2O / t (mole cc-1 sec-1) x 10^12
596.0°C
580.7
566.5 °C
549.9°
2000
4000
6000
600
1200
1800
150
300
450
600
750
TIME (sec)

Figure 14

Arrhenius plots for nitrous oxide production

● 15.5 % mixture

o 45.5 % mixture



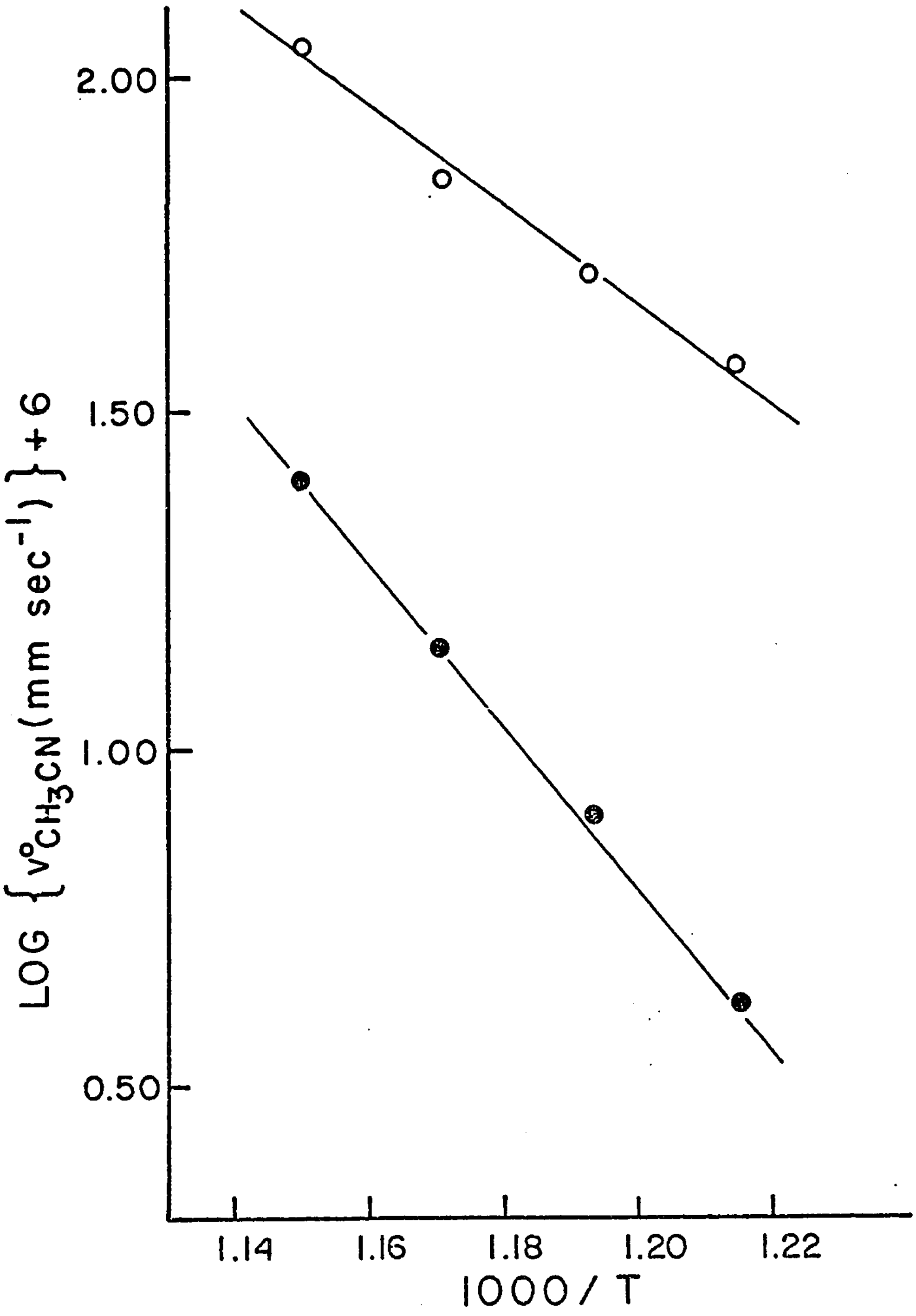
LOG $\{v^{\circ}_{N_2O}(mm\ sec^{-1})\} + 5$
2.00
1.50
1.00
0.50
1.14
1.16
1.18
1.20
1.22
1000/T

Figure 15

Arrhenius plots for acetonitrile production

● 15.7 % mixture

o 45.5 % mixture


2.00
1.50
1.00
0.50
1.14
1.16
1.18
1.20
1.22
1000 / T
LOG $\{v^{\circ}_{CH_3CN}(\text{mm sec}^{-1})\}+6$

production of nitrous oxide is 67 kcal mole^{-1} and that of acetonitrile is 55 kcal mole^{-1}. For the 45.5 % mixture the activation energies are 47 kcal mole^{-1} and 35 kcal mole^{-1}, respectively.

F. The Production of Water and Nitrogen

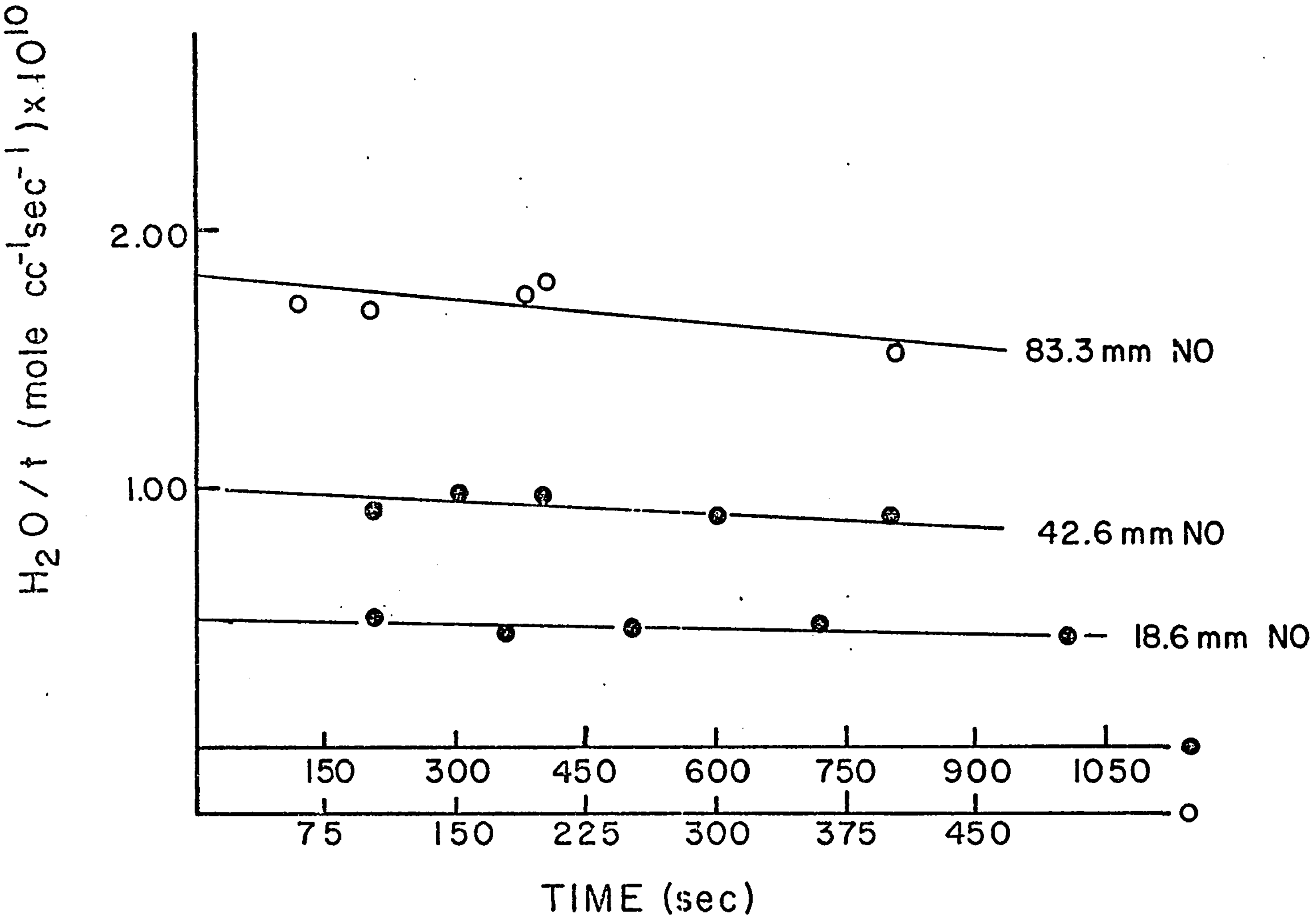
Examples of water and nitrogen production plots are presented in Figures 3 and 4. The rates of production of these products decreased with increasing conversion. At very high concentrations of NO, however, it seems that the production of nitrogen increased as the conversion increased (Figure 4). Typical rate-time plots are shown in Figures 16 and 17. In most cases rates derived from runs at low conversions were indistinguishable from initial rates. For water this was partly due to the scatter of the results, which did often not warrant an extrapolation. Order plots are presented in Figures 7 and 8. The orders with respect to ethane and nitric oxide were constant within experimental error at all pressures.

Arrhenius plots for water and nitrogen are given in Figures 18 and 19, respectively. The activation energies are 55 kcal mole^{-1} and 49 kcal mole^{-1}, respectively and are practically independent of the composition of the mixture.

Figure 16

Typical rate-time plots for the production of water.

Data were obtained for 100.0 mm C_2H_6 and varying pressures of NO at 596° C.



H_2O/t (mole cc^{-1}sec^{-1})x10^{10}
2.00
1.00
83.3 mm NO
42.6 mm NO
18.6 mm NO
150
300
450
600
750
900
1050
75
150
225
300
375
450
TIME (sec)

Figure 17

Typical rate-time plots for the production of nitrogen.

Data were obtained for 83.3 mm NO and varying pressures of C_2H_6 at 596° C.

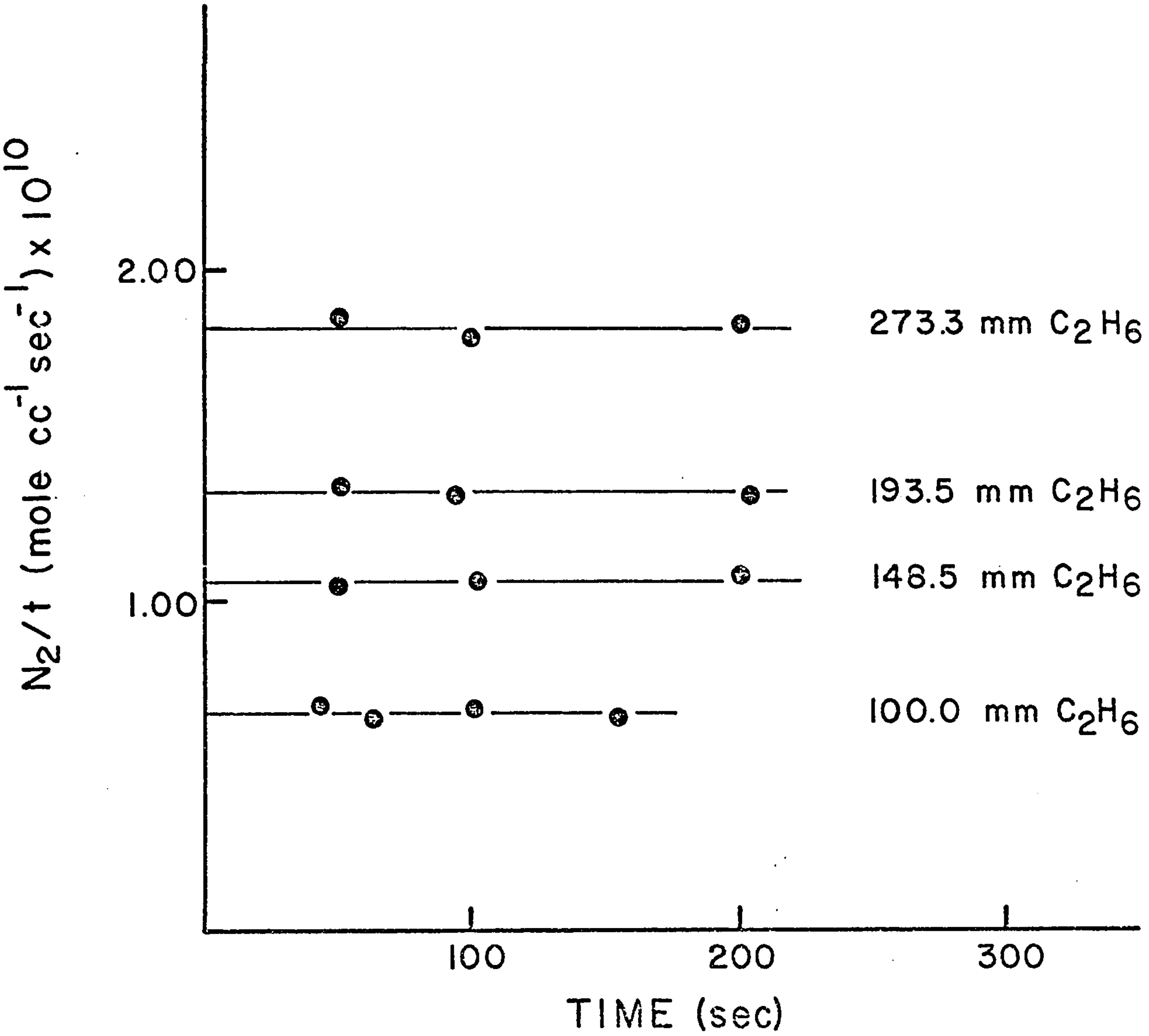
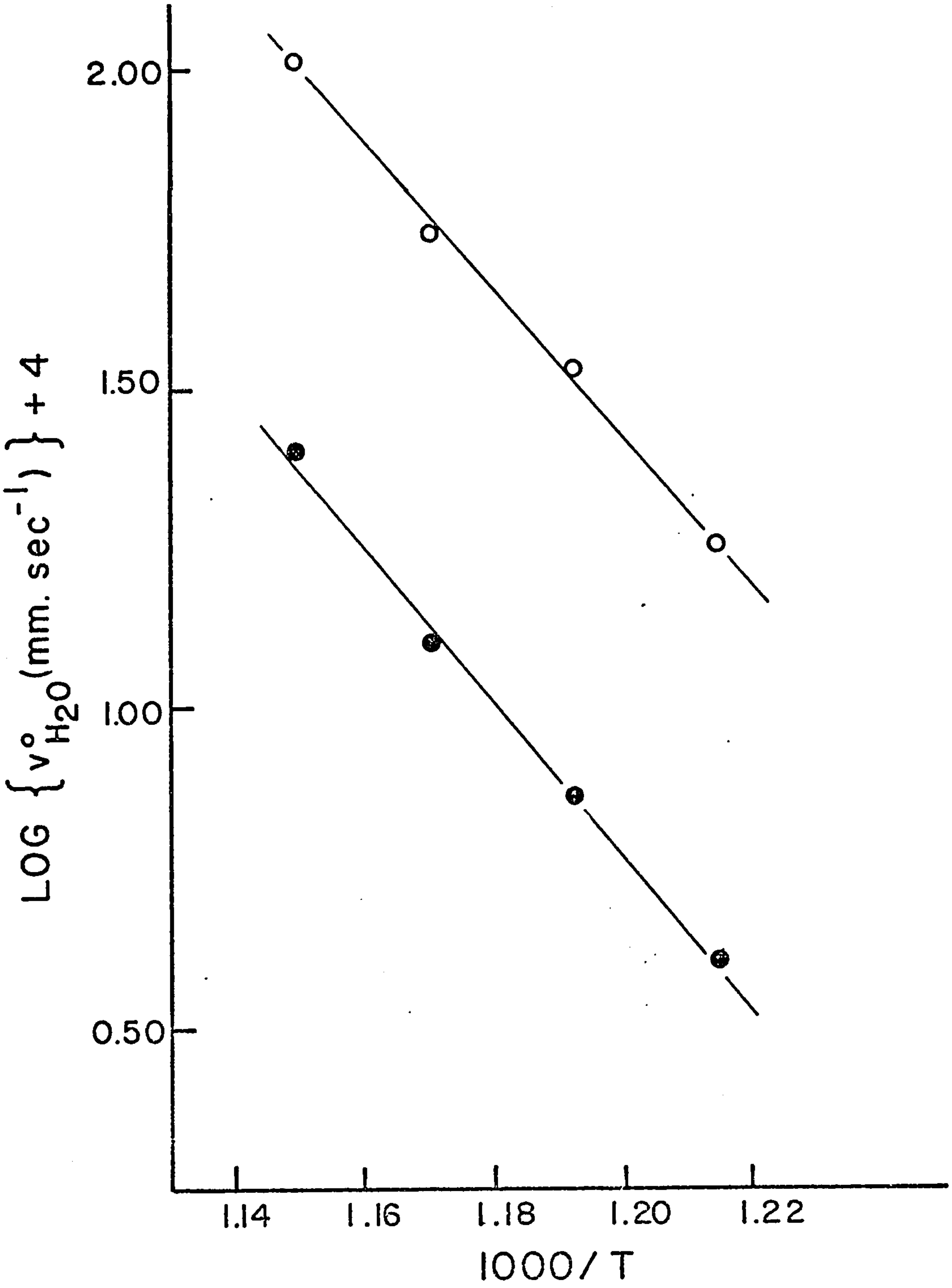

N_2/t (mole cc^{-1} sec^{-1}) x 10^{10}
2.00
1.00
273.3 mm C_2H_6
193.5 mm C_2H_6
148.5 mm C_2H_6
100.0 mm C_2H_6
100
200
300
TIME (sec)

Figure 18

Arrhenius plots for water production

● 15.7 % mixture

o 45,5 % mixture



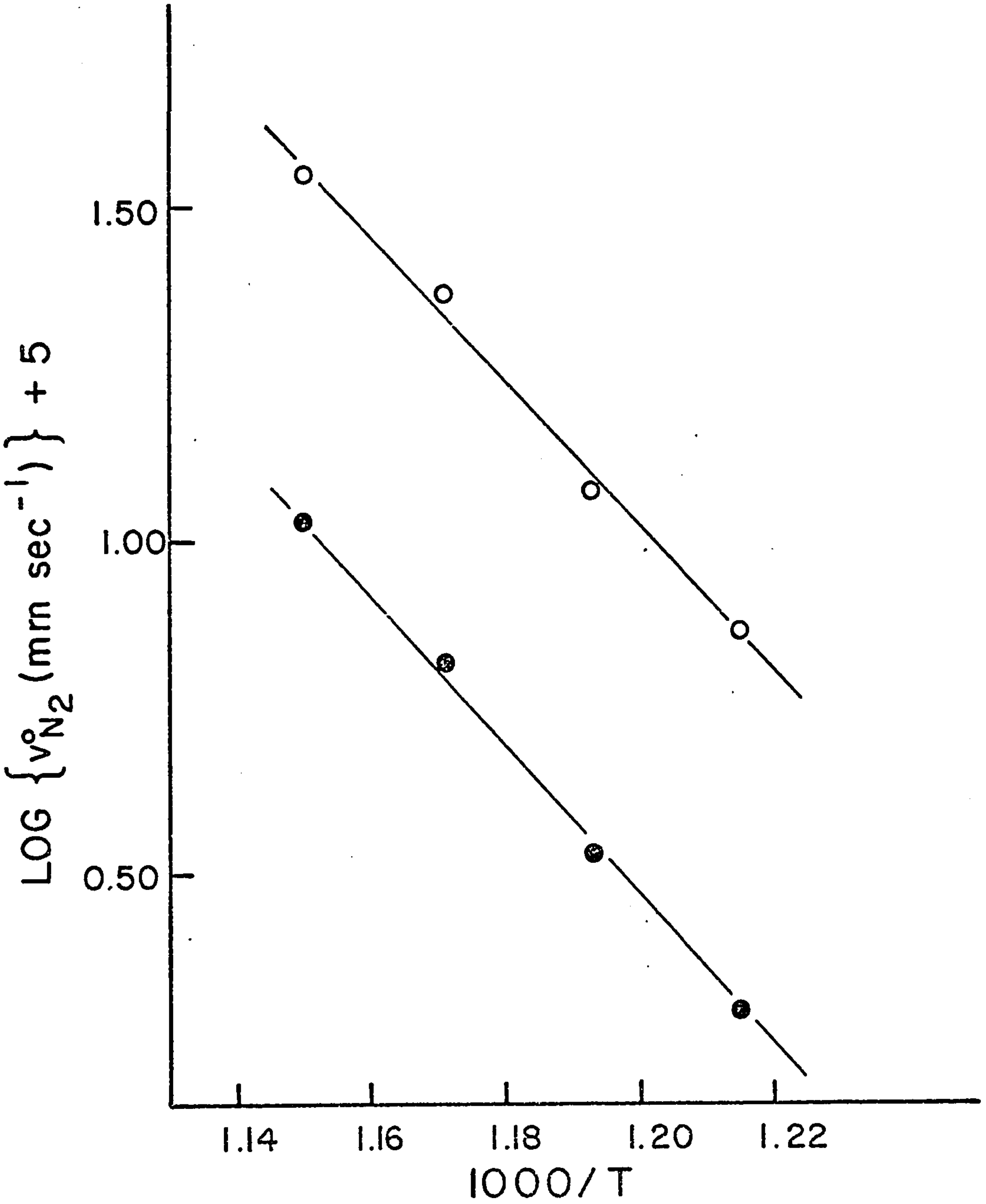
LOG $\{v^\circ_{H_2O}(\text{mm. sec}^{-1})\} + 4$
2.00
1.50
1.00
0.50
1.14
1.16
1.18
1.20
1.22
1000/T

Figure 19

Arrhenius plots for nitrogen production

● 15.7 % mixture

o 45.5 % mixture



LOG $\{v^{o}_{N_2}$ (mm sec^{-1})$\}$ + 5
1.50
1.00
0.50
1.14
1.16
1.18
1.20
1.22
1000/T

G. The Production of Methane

Typical examples of methane production plots are presented in Figures 3 and 4. The rates for this product always increased as the reaction progressed. Typical rate-time plots are shown in Figure 20. Often initial rates could be calculated from individual runs at low conversions. A double logarithmic plot of $v^o_{CH_4}$ vs. $P^o_{C_2H_6}$ is given in Figure 7. The order is constant at all pressures. Double logarithmic plots of $v^o_{\Delta CH_4}$ vs. $P^o_{C_2H_6}$ and P^o_{NO}, where $v^o_{\Delta CH_4}$ is the total rate of methane production minus that in the absence of nitric oxide, are shown in Figures 7 and 8. Again the orders are constant at all pressures.

Arrhenius plots for methane are presented in Figure 21. The activation energy is 74 kcal mole^{-1} for the 15.7 % mixture and 68 kcal mole^{-1} for the 45.5 % mixture.

H. The Inhibition Curves

The initial rates of all primary products were obtained for mixtures containing 100 mm C_2H_6 and varying pressures of NO. These rates plotted as functions of NO pressure are shown in Figure 22. All products derived from the consumption of nitric oxide have zero rates at zero nitric oxide pressure. The rate of ethylene production has a minimum at about 15 mm NO and that of hydrogen production

Figure 20

Typical rate-time plots for the production of methane.

Data were obtained for 83.3 mm NO and varying pressures of C_2H_6 at 596° C.

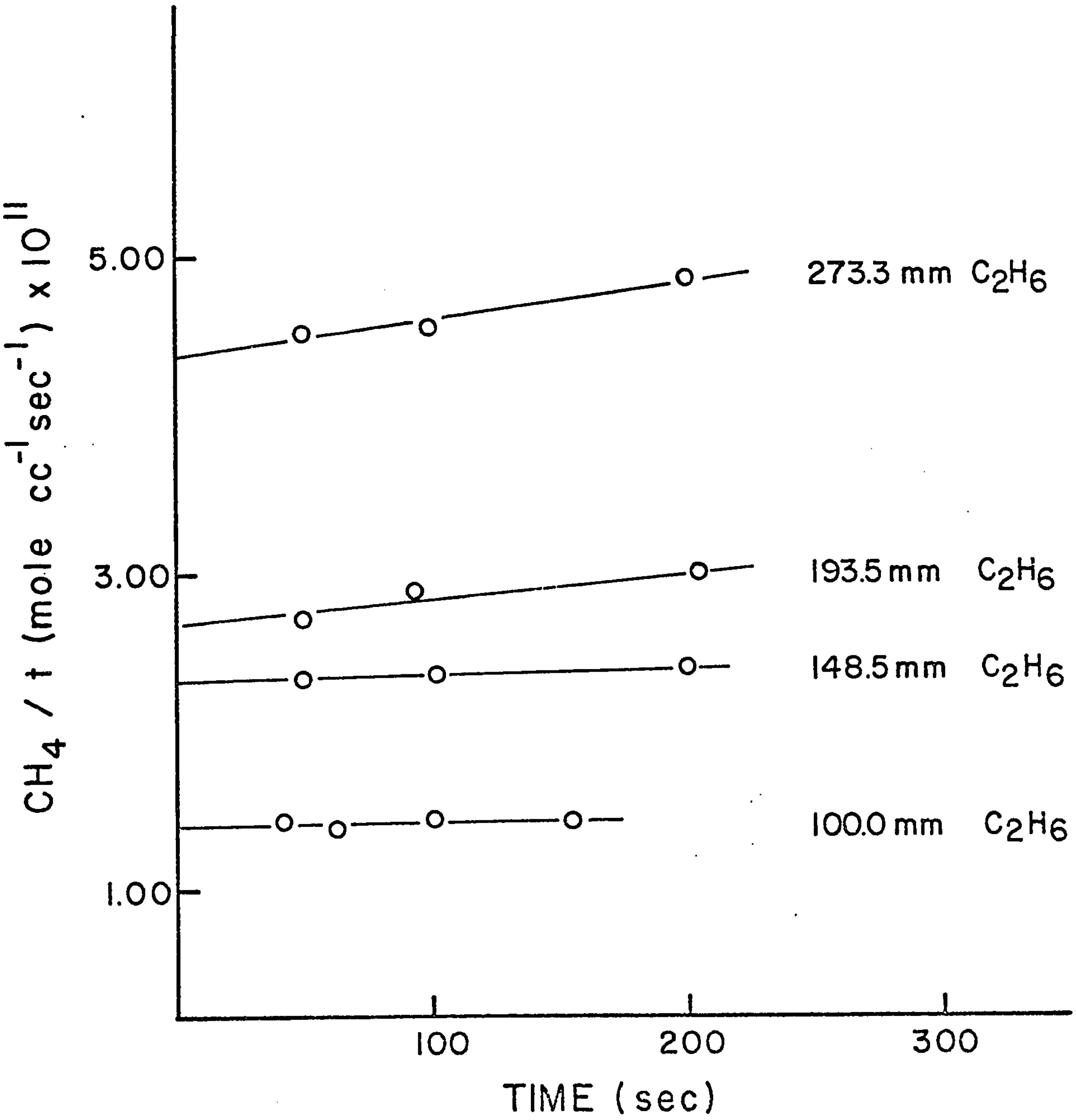

CH_4 / t (mole cc^{-1} sec^{-1}) x 10^{11}
5.00
3.00
1.00
100
200
300
TIME (sec)
273.3 mm C_2H_6
193.5 mm C_2H_6
148.5 mm C_2H_6
100.0 mm C_2H_6

Figure 21

Arrhenius plots for methane production

● 15.7 % mixture

o 45.5 % mixture

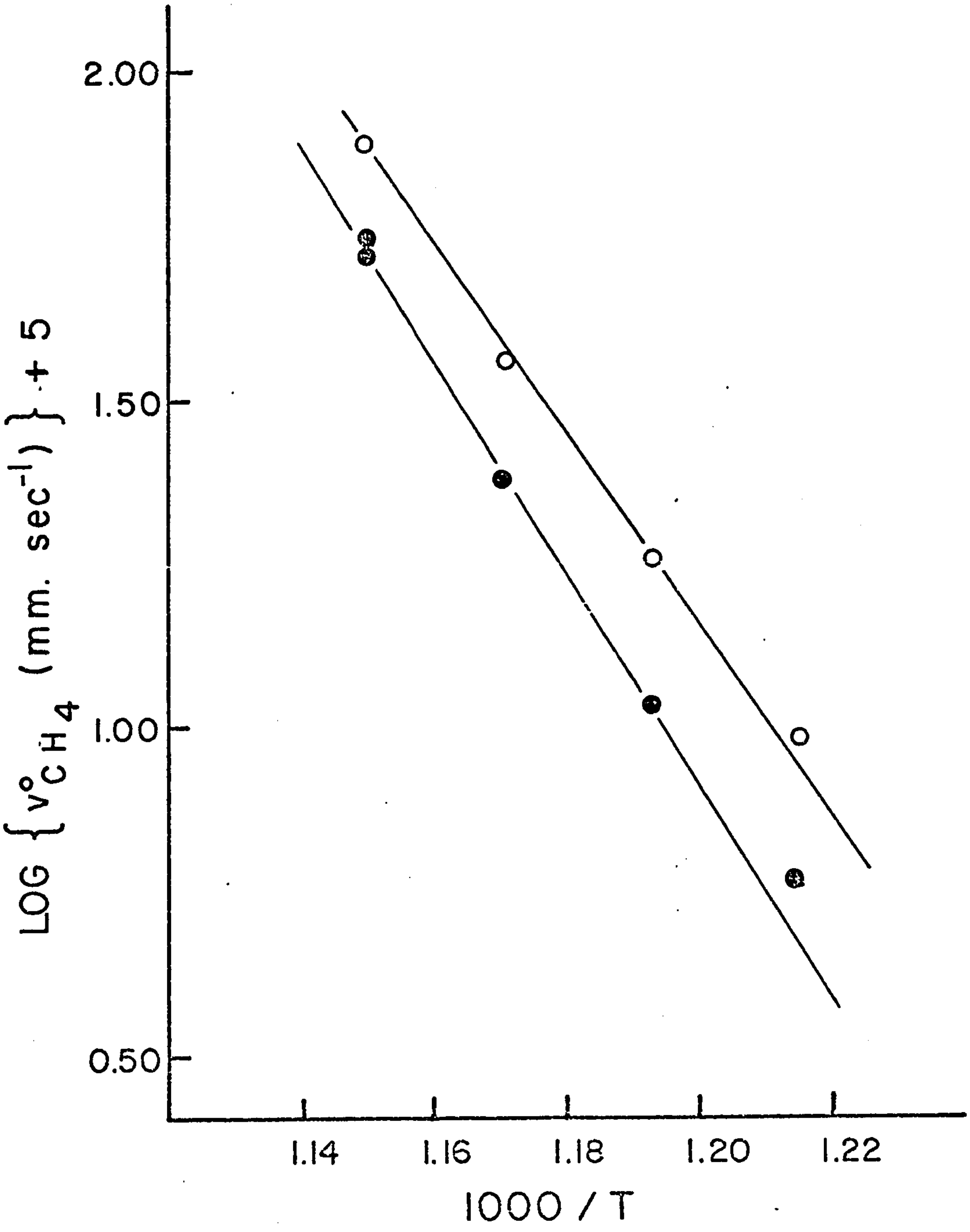
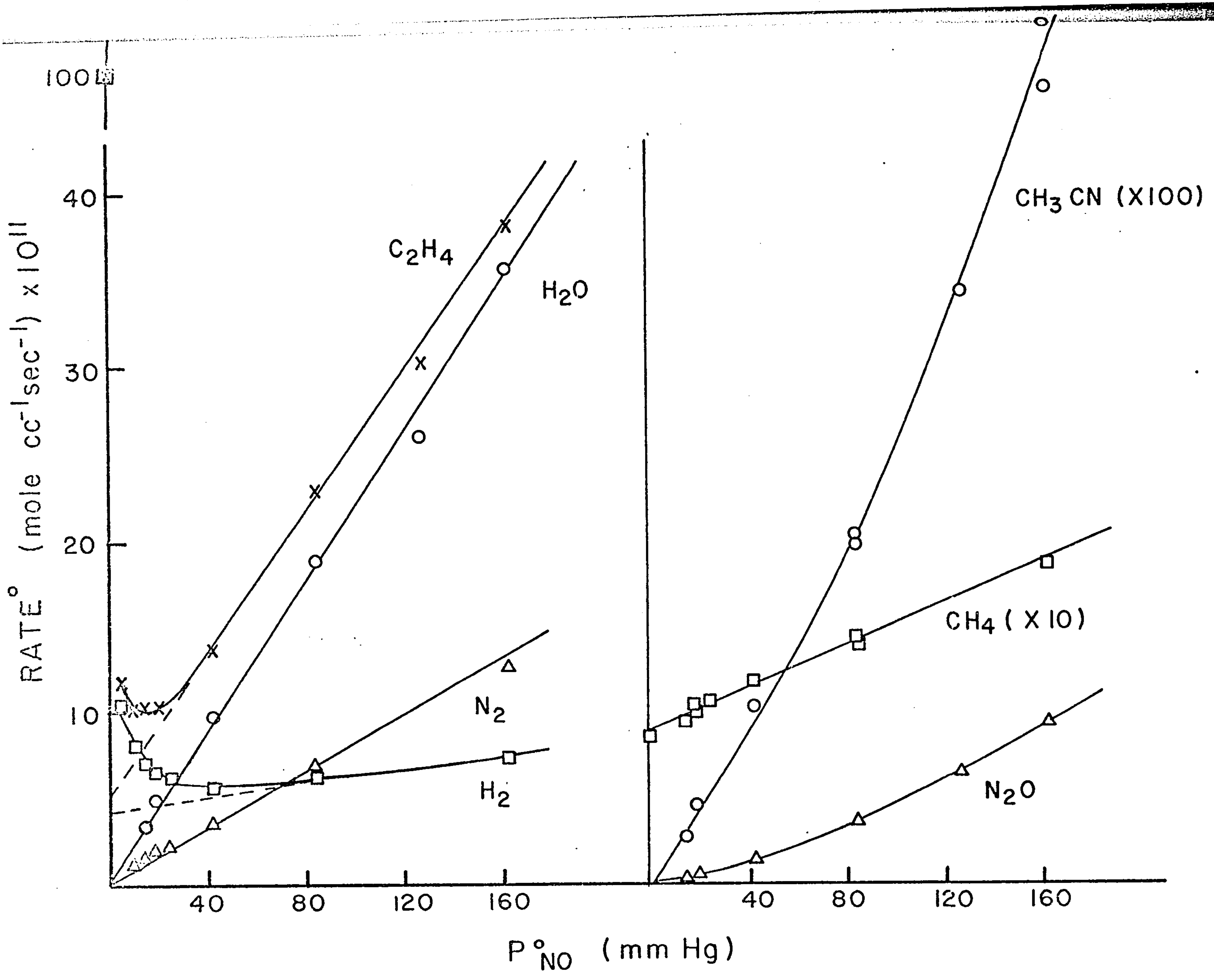

2.00
1.50
1.00
0.50
LOG {v°CH4 (mm. sec-1)} + 5
1.14
1.16
1.18
1.20
1.22
1000 / T

Figure 22

Initial rates of formation of ethylene, water, hydrogen, nitrogen, nitrous oxide, methane and acetonitrile as functions of nitric oxide pressure at 596° C.

Data were obtained with 100.0 mm C_2H_6 and varying pressures of NO.


100
40
30
20
10
RATE° (mole cc^{-1}sec^{-1}) x 10^{11}
C_2H_4
H_2O
N_2
H_2
CH_3CN (X100)
CH_4 (X 10)
N_2O
40
80
120
160
40
80
120
160
P°_{NO} (mm Hg)

has a minimum at about 43 mm. The straight line portions of these curves at higher NO pressures extrapolate to 5.15×10^{11} (mole cc^{-1} sec^{-1}) and to 4.43×10^{-11} (mole cc^{-1} sec^{-1}), respectively. The methane rate, which is a linear function of NO, extrapolates to the value obtained in the absence of NO.

I. The Consumption of Nitric Oxide

For some C_2H_6-NO mixtures the consumption of NO was directly measured at 596° C by observing the decrease in concentration as described in the experimental section. Some examples are presented in Figure 23 and Table 2.

There is good agreement between the consumption directly measured and the appearance of nitrogen in the products.

J. The Production of Secondary Products

Several secondary products, which occur under all conditions, were detected and occasionally measured. Some typical yield-time plots of carbon monoxide are presented in Figure 24. The production of CO has always a relatively short induction period.

Some yield-time plots of hydrogen cyanide and acetaldehyde production are shown in Figure 25. There are long induction periods, of about equal length, for the formation of these products.

Figure 23

Consumption of nitric oxide at 596° C

○ Data were obtained from a mixture containing 18.6 mm NO and 100.0 mm C_2H_6.

● Data were obtained from a mixture containing 14.6 mm NO and 100.0 mm C_2H_6.

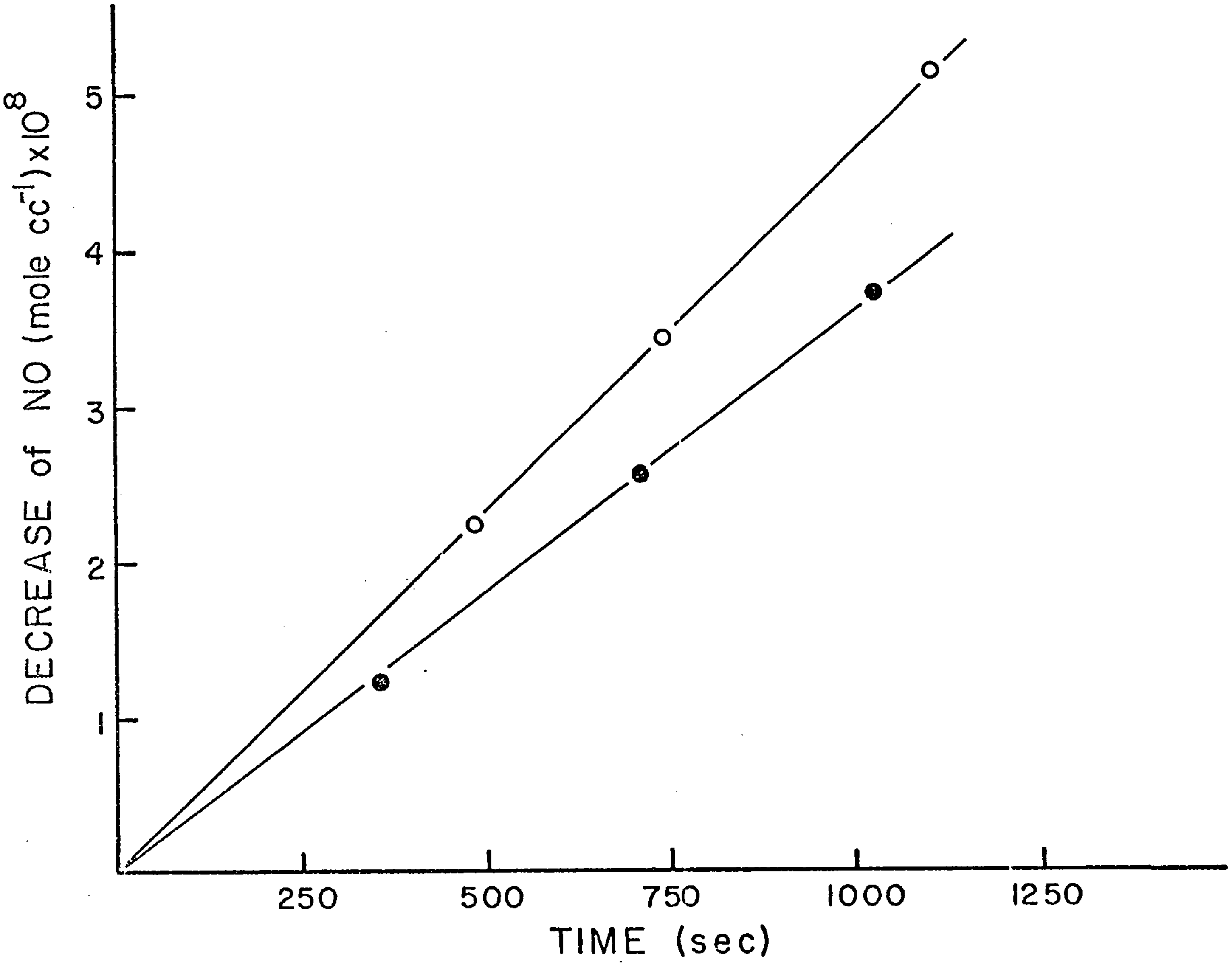

5
4
3
2
1
DECREASE of NO (mole cc^{-1})x10^8
250
500
750
1000
1250
TIME (sec)

Table 2

Rates of consumption of nitric oxide at 596° C for two different C_2H_6-NO mixtures.

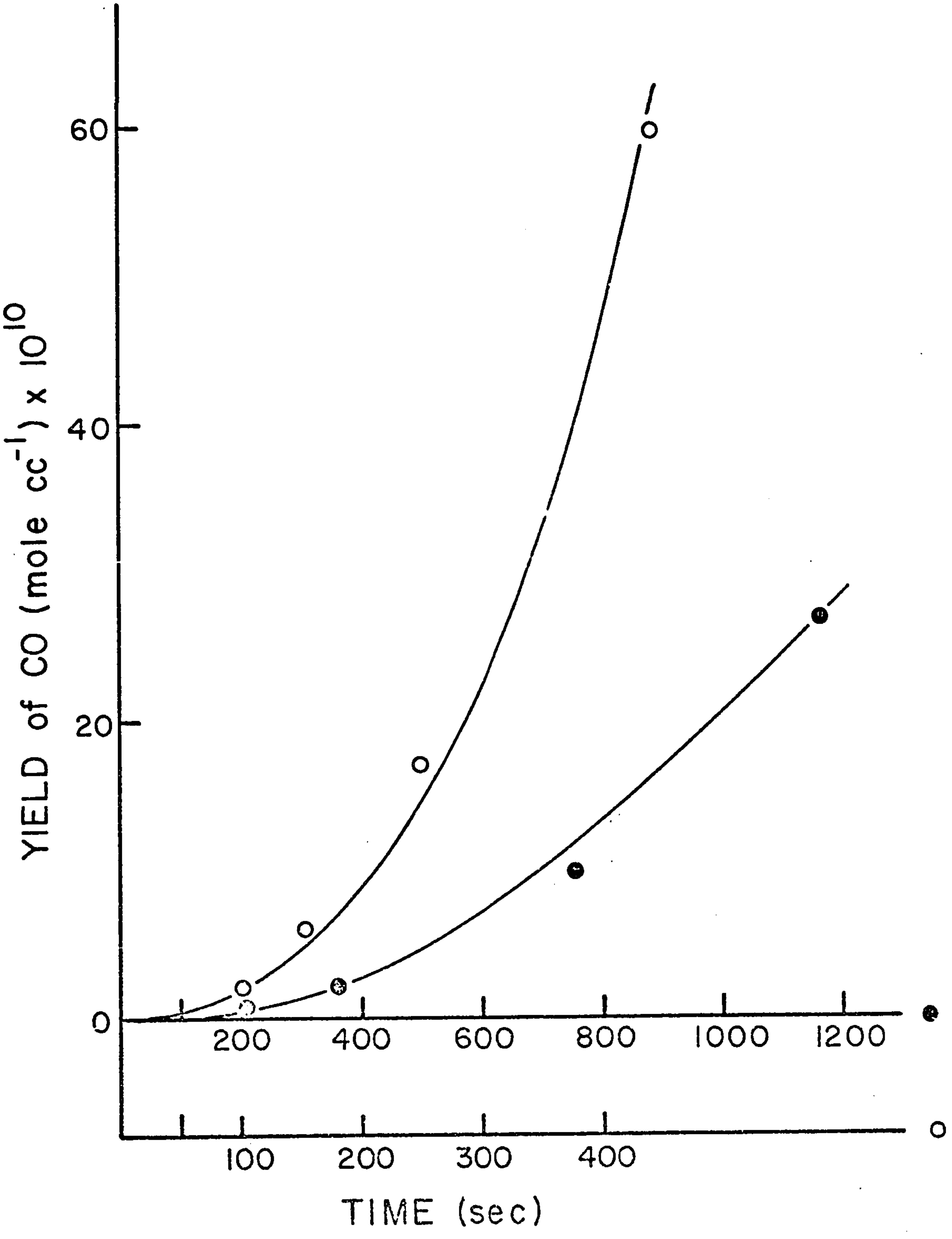
$P^o_{C_2H_6}$ mm Hg	P^o_{NO} mm Hg	$-v^o_{NO}$ mole $cc^{-1}sec^{-1}$	$2\ v^o_{N_2} + 2\ v^o_{N_2O}$ mole $cc^{-1}sec^{-1}$
100.0	14.6	3.62×10^{-11}	3.45×10^{-11}
100.0	18.6	4.65×10^{-11}	4.44×10^{-11}

Figure 24

Yield-time plots for the production of carbon monoxide at 596° C.

● Results for 18.6 mm NO and 100.0 mm C_2H_6

c Results for 162 mm NO and 100.0 mm C_2H_6



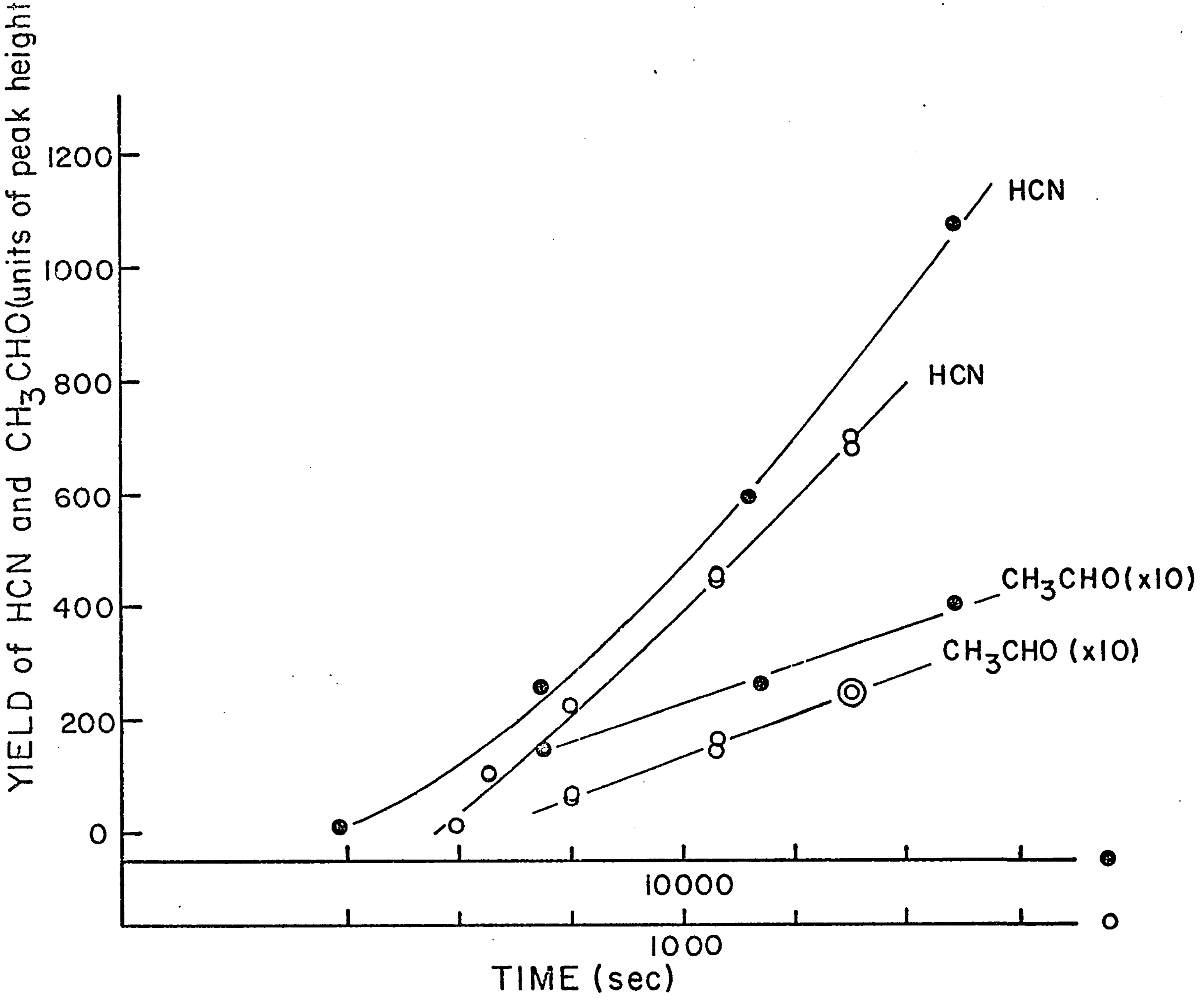
YIELD of CO (mole cc^{-1}) x 10^{10}
60
40
20
0
200
400
600
800
1000
1200
●
100
200
300
400
○
TIME (sec)

Figure 25

Yield-time plots for the production of hydrogen cyanide and acetaldehyde.

○ Data were obtained with 42.6 mm NO and 100.0 mm C_2H_6 at 596° C.

● Data were obtained with 18.6 mm NO and 100.0 mm C_2H_6 at 549.9° C.


YIELD of HCN and CH_3CHO(units of peak height)
0
200
400
600
800
1000
1200
HCN
HCN
CH_3CHO(x10)
CH_3CHO (x10)
10000
1000
TIME (sec)

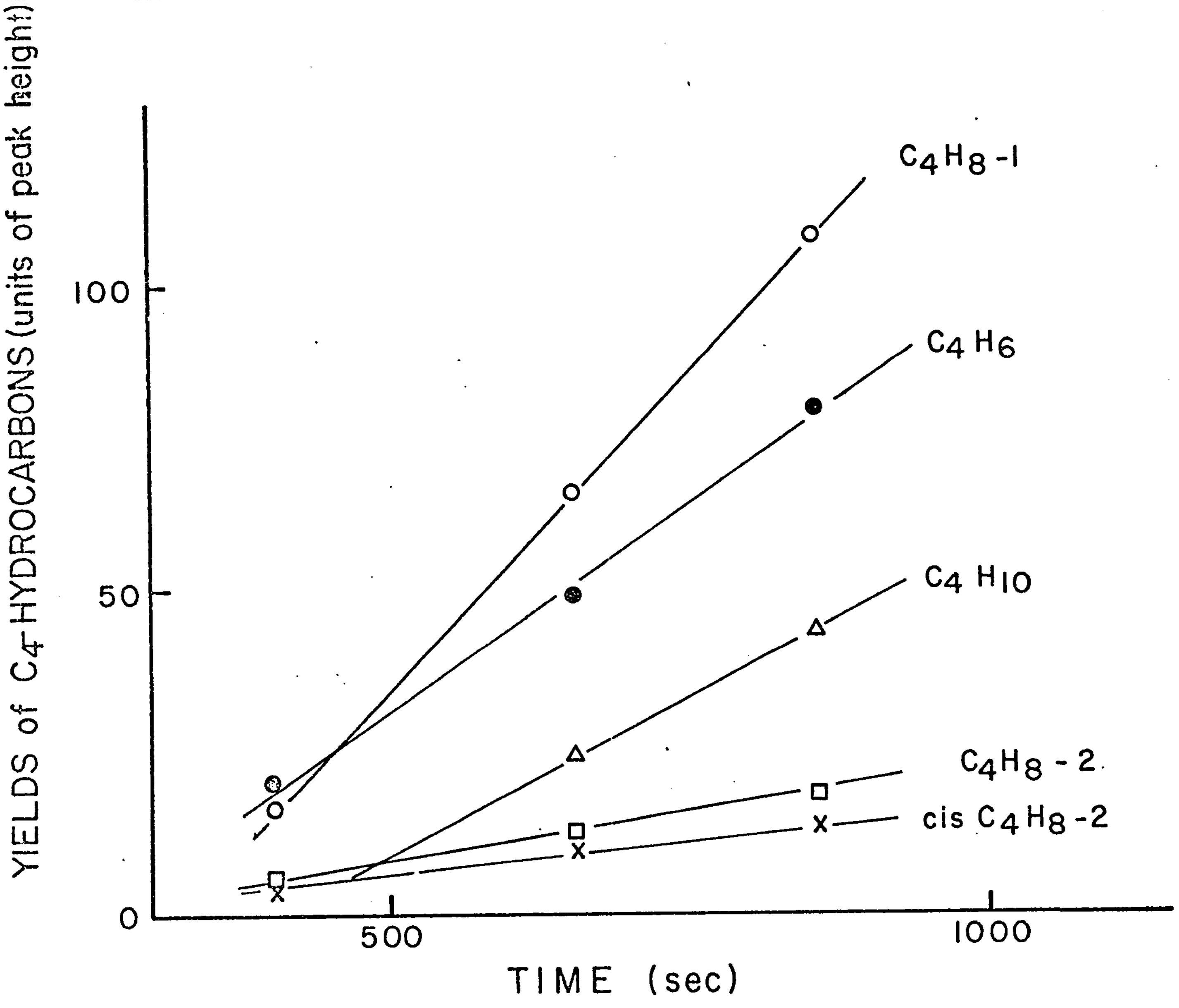
Several C_4-hydrocarbons are also secondary products. An example of yield-time curves is given in Figure 26. The induction periods of butene-1, butadiene-1,3, n-butane and cis- and trans-butene-2 are all different. Generally, they are longer than that for CO, but shorter than those for HCN and CH_3CHO.

Figure 26

Yield-time plots for the production of C_4-hydrocarbons:

○ butene-1, ● butadiene-1,3, △ n-butane, □ trans-butene-2, x cis-butene-2.

Data were obtained with 83.3 mm NO and 193.5 mm C_2H_6 at 596° C.


YIELDS of C_4-HYDROCARBONS (units of peak height)
100
50
0
500
1000
TIME (sec)
C_4H_8-1
C_4H_6
C_4H_{10}
C_4H_8-2
cis C_4H_8-2

$$[C_2H_5] = \left(\frac{k_1}{k_5}\right)^{1/2} [C_2H_6]^{1/2}$$

$$[H] = \frac{k_3}{k_4} \left(\frac{k_1}{k_5}\right)^{1/2} \frac{1}{[C_2H_6]^{1/2}}$$

Using the experimental rates of Table 1 and the kinetic parameters for reactions 2, 4 and 5 of Table 3 one can calculate the following steady-state concentrations for 100 mm C_2H_6 and 596° C:

$$[CH_3] = 9.5 \times 10^{-15} \text{ mole cc}^{-1}$$
$$[C_2H_5] = 4.6 \times 10^{-13} \text{ mole cc}^{-1}$$
$$[H] = 1.1 \times 10^{-15} \text{ mole cc}^{-1}$$

This shows that the concentration of ethyl radicals is about 100 times larger than that of hydrogen atoms or methyl radicals.

In the presence of nitric oxide the above reactions will still take place. If the NO combines with radicals, one would expect it to have a more important effect on the concentration of ethyl radicals than on the concentration of the other two radicals; the concentration of ethyl radicals is much larger and the combination of NO with H or CH_3 will need a third body. Heicklen and Cohen (25) reviewed the experimental evidence for the reactions:

Table 3

Kinetic parameters for elementary reactions

Reactions	Frequency Factor (sec^{-1} or cc $mole^{-1}sec^{-1}$ or cc^2 $mole^{-2}$ sec^{-1})	Activation Energy (kcal $mole^{-1}$)	References
$C_2H_6 \xrightarrow{k_1} 2\ CH_3$	1.0×10^{16}	86.0	Lin and Back (15)
$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$	2.0×10^{11}	10.4	Trotman-Dickenson et al. (75)
$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$	3.8×10^{13}	38.0	Lin and Back (76)
$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$	1.5×10^{14}	9.9	Thrush (77)
$2\ C_2H_5 \xrightarrow{k_5} C_4H_{10}$	2.0×10^{13}	0	Schepp and Kutschke(78)
$C_2H_5 + NO \xrightarrow{k_6} C_2H_5NO$	10^{11}	0	Estimate based on review by Heicklen and Cohen(25)
$CH_3 + NO(+M) \xrightarrow{k_i} CH_3NO$	10^{16}	0	Estimate based on review by Heicklen and Cohen(25)
$H + NO + M \xrightarrow{k_{ii}} HNO + M$	2×10^{16}	0	Estimate based on review by Heicklen and Cohen(25)
$C_2H_5NO + 2\ NO \xrightarrow{k_{iii}} C_2H_5 + N_2 + NO_3$	1.9×10^{6}	-2.9	Christie et al. (31)
$C_2H_5NO \xrightarrow{k_6} CH_3CH{=}NOH$	10^{13}	40	Batt and Gowenlock (40)
$OH + C_2H_6 \xrightarrow{k_{11}} H_2O + C_2H_5$	10^{14}	3.6	Horne and Norrish (79)

$$C_2H_5 + NO \xrightarrow{6} C_2H_5NO$$

$$CH_3 + NO\ (+M) \xrightarrow{i} CH_3NO\ (+M)$$

$$H + NO + M \xrightarrow{ii} HNO + M$$

Most studies refer to room temperature. The experimental rate constants vary considerably for reaction i and no really reliable value is known. The rate constant for reaction ii seems to be the most accurately known of the three. Some approximate values, which apply perhaps to the experimental conditions of this work, are given in Table 3. This enables one to get an estimate of the effect of NO on reactions 2, 3 and 4. For 596°C, e.g., one obtains:

$$\frac{v_2}{v_i} = \frac{k_2\ [CH_3]\ [C_2H_6]}{k_i\ [CH_3]\ [NO]\ [M]} \doteq \frac{4.85 \times 10^{-8}}{[NO]}$$

$$\frac{v_3}{v_6} = \frac{k_3\ [C_2H_5]}{k_6\ [C_2H_5]\ [NO]} \doteq \frac{2.19 \times 10^{-8}}{[NO]}$$

$$\frac{v_4}{v_{ii}} = \frac{k_4\ [H]\ [C_2H_6]}{k_{ii}\ [H]\ [NO]\ [M]} \doteq \frac{2.4 \times 10^{-5}}{[NO]}$$

For a 15.7 % mixture - consisting of 100.0 mm C_2H_6 and 18.6 mm NO - one has then:

$$\frac{v_2}{v_i} = \frac{4.85 \times 10^{-8}}{3.43 \times 10^{-7}} \doteq 1.4 \times 10^{-1}$$

$$\frac{v_3}{v_6} = \frac{2.19 \times 10^{-8}}{3.43 \times 10^{-7}} \doteq 6.4 \times 10^{-2}$$

$$\frac{v_4}{v_{ii}} = \frac{2.4 \times 10^{-5}}{3.43 \times 10^{-7}} \doteq 7.0 \times 10$$

These results suggest that the scavenging of CH_3 and C_2H_5 radicals is efficient, but not that of H atoms. That reaction 6 is competitive with reaction 3 is certainly supported by the experimental evidence of the present work. For the above mixture v_3 drops at least to about 10 % of the rate in the absence of NO, and for a 1.56 % mixture the concentration of C_2H_5 is already so reduced that v_5 is at most only 2 % of that in the absence of NO. In mixtures containing larger amounts of nitric oxide v_5 is entirely negligible. The concentration of CH_3, however, does not seem to be decreased by the presence of NO, since the rate of formation of methane actually increased as a function of NO. In fact, the rate of formation of methane (Figure 22) when extrapolated to zero NO pressure yields the rate of the uninhibited methane formation. The most plausible explanation for this behavior is that reaction i is not at all competitive with reaction 2 and that there is some additional source of CH_3 radicals. It seems then that some of the previously determined third-order rate constants for i are too high by at least a factor of 100.

One striking feature of the present results, shown in Figure 22, is that the rates of hydrogen and ethylene production vary in different ways with pressure of NO. Both rates fall sharply to a minimum with addition of NO and then increase again with increasing NO. The rate of hydrogen formation, however, does not rise as steeply as that of ethylene formation. Further, the minima are numerically not the same and occur at different nitric oxide pressures. Since the rate of hydrogen formation is always lower than that of ethylene formation, reactions 3 and 4 cannot be the only ones leading to the formation of these products. Further, the rates of formation of these products, extrapolated from high NO pressures to zero NO pressure, lead to about the same intercept. Since both rates are functions of the type

$$v = a/[NO] + b + c\ [NO]$$

for a given ethane pressure, this intercept would be a measure of the reactions 3 and 4. This point will be taken up later. Abstraction of an H atom from C_2H_5 by NO is another possible reaction, viz.

$$C_2H_5 + NO \xrightarrow{7} C_2H_4 + HNO.$$

At high temperatures HNO will dissociate according to

$$HNO + M \xrightarrow{8} H + NO + M.$$

As will be shown later, the occurrence of these two reactions can explain the rise in rate of production of hydrogen as the NO pressure increases.

II. Elementary Reactions that Lead to Products which Contain Nitrogen and Oxygen.

One surprising finding of this work is that the rates of decomposition of NO are considerable. Even at the lowest concentration of NO, nitrogen- and oxygen-containing compounds are formed, and there does not seem to be any fundamental difference between mixtures containing little or much nitric oxide. Table 4 shows that even at low NO pressures the rate of disappearance of nitric oxide is not much lower than that of ethane. In fact, considering that in such mixtures there is less NO than C_2H_6, one sees that the percentage decomposition of NO is even larger than that of C_2H_6 for a given contact time. At very high NO pressures the reverse is true. Thus it appears that both substances have to be considered as reactants. The rates of disappearance of the two reactants were calculated from the rates of product formation obtained at 596°C. The ethane pressure was constant at 100 mm Hg.

Since the nitric oxide decomposes practically as fast as the ethane, one must assume that the nitric oxide is somehow involved in the propagation steps of the ethane pyrolysis. In Chapter I a brief review was given of the possible reactions of RNO in the presence of NO. The reaction

$$RNO + 2\ R \longrightarrow R_2NOR$$

Table 4

Rates of disappearance of ethane and nitric oxide at 596° C as functions of nitric oxide pressure.

P^o_{NO} mm Hg	$-v^o_{C_2H_6} \times 10^{11}$ mole cc^{-1}sec^{-1}	$-v^o_{NO} \times 10^{11}$ mole cc^{-1}sec^{-1}	$\frac{-v^o_{C_2H_6}}{-v^o_{NO}}$
14.6	10.8	3.95	2.73
18.6	10.6	5.09	2.08
42.6	14.2	10.2	1.39
84.0	23.62	20.2	1.17
162.0	39.1	44.1	0.887

can be dismissed on the grounds that it is known to occur when the radical concentrations are high and the nitric oxide concentration is low. The reaction

$$RNO + NO \longrightarrow RO + N_2O$$

can also be discounted, since one would expect primary products arising from RO; in this work RO would be C_2H_5O and one would expect reactions such as

$$C_2H_5O \longrightarrow CH_3CHO + H$$

$$C_2H_5O + NO \longrightarrow CH_3CHO + HNO$$

$$C_2H_5O + C_2H_6 \longrightarrow C_2H_5OH + C_2H_5\cdot.$$

CH_3CHO and C_2H_5OH, however, were not detected as primary products. The most likely reactions are

$$C_2H_5NO + 2\ NO \xrightarrow{iii} C_2H_5 + N_2 + NO_3$$

$$C_2H_5NO \xrightarrow{6'} CH_3CH{=}NOH.$$

Christie and coworkers (31) determined the rate parameters for reaction iii. No accurate rate parameters for reaction 6' are known. Batt and Gowenlock (40), however, studied the isomerization of CH_3NO and estimated the rate constant for the homogeneous reaction to be approximately given by

$$k = 10^{13} \exp\left[-40000/RT\right].$$

If we assume that the rate parameters are similar for the nitrosoethane isomerization, we get the following comparison:

$$\frac{v_{iii}}{v_6} = \frac{[C_2H_5NO]\ [NO]^2\ \times 1.9 \times 10^6\ e^{2900/RT}}{[C_2H_5NO]\ \times\ 10^{13}\ e^{-40000/RT}}\ .$$

For a mixture of 162 mm NO and 100 mm C_2H_6 at 596° C we then have

$$\frac{v_{iii}}{v_6'} = 1.11 \times 10^{-7} .$$

Since the activation energy for the isomerization of the nitrosoethane is probably lower, and since this energy may be partly supplied by the energy released when C-NO bond formation takes place (41), reaction 9 can be neglected. Hence, it seems that isomerization to the corresponding oxime is the most likely fate of nitrosoethane. That the nitroso compound is short-lived is also borne out by the fact that such conceivable reactions as

$$C_2H_5NO + C_2H_5 \longrightarrow C_4H_{10} + NO$$

do not occur under the experimental conditions of this study. One difficulty with developing a mechanism for the NO-C_2H_6 system is that no information is apparently available on the bond energies of the oxime molecule. However, it seems safe to assume that the most reactive bonds are the double bond and the -OH bond.

Some light is thrown on the possible fate of the acetaldoxime by the previous studies of Pratt and Purnell (46, 47) who studied the pyrolysis of acetaldoxime at temperatures between 330 and 440° C. They obtained a wide range of products and found that the decomposition had an explosion limit at 440° C. A short induction period could be eliminated by adding 1 % NO. Adding 7 % NO to the oxime increased the rate of decomposition by a factor of 6. Therefore, they suggested that in the absence of NO

$$CH_3CH{=}NOH \xrightarrow{iv} CH_3CHN\cdot + OH$$

is the initiation step in the decomposition, whereas at higher NO concentrations

$$NO + CH_3CHNOH \xrightarrow{9} CH_3CHN\cdot + HNO_2$$

is the only important initiation.

Later Pratt (80) found in a mass-spectrometric study that

$$[CH_3CH = NOH + C_2H_5NO] \;/\; [C_2H_6] = 2 \times 10^{-7}\ .$$

This result was obtained under experimental conditions quite close to those of this work. This indicates that the oxime is readily removed.

In the region of higher NO concentrations the rate of production of H_2O is almost as great as that of C_2H_4. Since the concentration of C_2H_5 is quite low, as pointed out previously, one would suspect that reaction 3 cannot be the only one leading to the formation of C_2H_4, and that these large and similar rates of formation of C_2H_4 and H_2O spring from the same sequence of reactions. It is natural to suggest that these reactions are

$$M + HNO_2 \xrightarrow{10} HO + NO + M$$

$$OH + C_2H_6 \xrightarrow{11} H_2O + C_2H_5$$

Reactions 6', 9, 10 and 11 together regenerate the ethyl radical and explain the rapid consumption of NO. In view of the high velocity of reaction 11 (79) and the large concentration of C_2H_6, the OH radical is unlikely to react in any other way.

It seems that no information is available on the properties of the CH_3CHN radical. But it is known that the dimer, the acetaldazine, gives nitrogen and ethylene as the major products at high temperatures (81). Gowenlock and Haynes (82) found that the azine yields nitrogen and butene-2 as the major products at 600-700° K. It is possible that at higher temperatures (820-870° K) nitrogen and ethylene are the major products. In this work butene-2 was not detected as a primary product. Hence, one might suggest

$$2\ CH_3CHN\cdot \longrightarrow CH_3CHN\text{-}NCHCH_3 \longrightarrow 2\ C_2H_4 + N_2$$

or

$$2\ CH_3CHN\cdot \xrightarrow{12} 2\ C_2H_4 + N_2$$

as possible reactions of the CH_3CHN radical. Since not only nitrogen but also nitrous oxide is a major product at high NO pressures, one can suggest an analogous reaction for the formation of N_2O, viz.:

$$CH_3CHN\cdot + NO \xrightarrow{13} C_2H_4 + N_2O\ .$$

Reactions 9 to 13 predict that

$$v_{H_2O} = 2\ v_{N_2} + v_{N_2O}\ .$$

Further, since C_2H_4 and H_2 are produced in equal amounts by reaction 3 and 4, respectively, we also predict that

$$v_{C_2H_4} = v_{H_2O} + v_{H_2} \ .$$

Both relations are in excellent agreement with the experimental results, as will be shown later.

There are several reactions which can be postulated to explain the production of the minor amounts of acetonitrile which are formed:

$$2\ CH_3CHN \xrightarrow{14} CH_3CN + CH_3CH{=}NH$$
$$CH_3CHN + NO \xrightarrow{15} HNO + CH_3CN$$
$$CH_3CHNOH \xrightarrow{16} CH_3CN + H_2O \text{ or other products.}$$

A reaction analogous to 14 has recently (83, 84) been postulated for the radical CH_2N.

At this point it is perhaps appropriate to comment on the additional source of CH_3 radicals mentioned earlier. In their study of the acetaldoxime decomposition Pratt and Purnell (46, 47) proposed the reaction

$$CH_3CHN \longrightarrow CH_3 + HCN,$$

which would also be an obvious choice for the C_2H_6-NO system. This, however, is unlikely in this case, since HCN was not a primary product. It seems therefore that the only other likely source is the oxime. It is difficult to propose any detailed reaction, but writing formally

$$CH_3CH{=}NOH + NO \xrightarrow{17} CH_3 + \text{product(s)}$$

leads to the correct functional form of the rate expression. Since the amount of products arising from reaction 17 is small, one would not detect any deficiency in the mass balance.

III. Initiation and Termination Reactions

Reaction 1 certainly initiates the decomposition of the C_2H_6 - NO system. Nitric oxide alone was found not to decompose under the experimental conditions of this work. Hence, initiation cannot come from NO alone. But NO might react with C_2H_6 according to

$$C_2H_6 + NO \longrightarrow HNO + C_2H_5$$

and thereby contribute to the initiation of the pyrolysis. This had previously been postulated by Laidler and Wojciechowski, as discussed in Chapter I. It is difficult to say how important this reaction is, since no reliable information about it is available. The reaction might well complicate the C_2H_6 - NO pyrolysis, and it certainly will be important in systems involving more labile hydrogen atoms.

The nature of the termination reactions is more uncertain. Reaction 16 is a termination step, but not enough acetonitrile is formed to permit the conclusion that reaction 16 produces only this compound. As will later be discussed, the kinetics of formation of this product can be explained fairly well by the occurrence of reactions 14 and 15. Some products which could conceivably arise from the unimolecular decomposition or isomerization of the oxime are CH_3CONH_2, CH_4 + HN=CO, C_2H_2 + NH_2OH, CH_3N=CO + H_2, CH_2=C=NH + H_2O and CH_3NC + H_2O. Most of these would not be stable under the experimental conditions of this work and would react further. In particular one would expect CH_3CONH_2, CH_2=C=NH and CH_3NC to yield acetonitrile. Secondary production of CH_3CN does indeed take place, as evidenced by the steep slopes of the rate-time plots shown in Figure 12. Secondary production can only come from very unstable products, since the induction period seems to be extremely short. One cannot envisage such secondary production of acetonitrile to arise from such products as H_2, CH_4, N_2, N_2O, C_2H_4, H_2O.

Reaction 5 is negligible; no other alkanes except methane have been found, and this excludes recombination of alkyl radicals as important termination steps. In view of the velocities of reactions 4 and 11, H and OH drop out as entities involved in terminations.

Another possible termination step is

$$2\ HNO \xrightarrow{18} H_2O + N_2O\ .$$

No Arrhenius parameters for this reaction have been measured, but it is known (85) that this reaction occurs readily at room temperature and must therefore have a very low activation energy. At high temperatures, however, the dissociation of HNO into H and NO may become more important than the disproportionation. The reaction

$$\mathrm{H{-}NO} + \mathrm{C_2H_5} \xrightarrow{19} \mathrm{C_2H_6} + \mathrm{NO}$$

is also a possible chain-ending step; one cannot, of course, tell by product formation whether it occurs. The analogue to 19,

$$\mathrm{HO{-}NO} + \mathrm{C_2H_5} \longrightarrow \mathrm{HOC_2H_5} + \mathrm{NO}$$

must be insignificant, since no alcohol was detected.

IV. The Over-all Mechanism

A. Derivation of Rate Equations

The above suggestions lead to the following over-all mechanism:

$$\mathrm{C_2H_6} \xrightarrow{1} 2\ \mathrm{CH_3}$$

$$\mathrm{CH_3} + \mathrm{C_2H_6} \xrightarrow{2} \mathrm{CH_4} + \mathrm{C_2H_5}$$

$$(\mathrm{M}+)\ \mathrm{C_2H_5} \xrightarrow{3} \mathrm{C_2H_4} + \mathrm{H}\ (+\mathrm{M})$$

$$\mathrm{H} + \mathrm{C_2H_6} \xrightarrow{4} \mathrm{H_2} + \mathrm{C_2H_5}$$

$$2\ \mathrm{C_2H_5} \xrightarrow{5} \mathrm{C_4H_{10}} \text{ or } \mathrm{C_2H_4} + \mathrm{C_2H_6}$$

$$\mathrm{C_2H_5} + \mathrm{NO} \xrightarrow{6} \mathrm{C_2H_5NO} \xrightarrow{6'} \mathrm{CH_3CHNOH}$$

$$\mathrm{C_2H_5} + \mathrm{NO} \xrightarrow{7} \mathrm{HNO} + \mathrm{C_2H_4}$$

$$\mathrm{HNO} + \mathrm{M} \xrightarrow{8} \mathrm{H} + \mathrm{NO} + \mathrm{M}$$

$$\mathrm{CH_3CHNOH} + \mathrm{NO} \xrightarrow{9} \mathrm{HNO_2} + \mathrm{CH_3CHN}$$

$$\mathrm{HNO_2} + \mathrm{M} \xrightarrow{10} \mathrm{OH} + \mathrm{NO} + \mathrm{M}$$

$$OH + C_2H_6 \xrightarrow{11} H_2O + C_2H_5$$

$$2\ CH_3CHN \xrightarrow{12} 2\ C_2H_4 + N_2$$

$$CH_3CHN + NO \xrightarrow{13} N_2O + C_2H_4$$

$$2\ CH_3CHN \xrightarrow{14} CH_3CN + CH_3CHNH$$

$$CH_3CHN + NO \xrightarrow{15} HNO + CH_3CN$$

$$CH_3CHNOH \xrightarrow{16} CH_3CN + H_2O \text{ or other products}$$

$$CH_3CHNOH + NO \xrightarrow{17} CH_3 + \text{product(s)}$$

$$2\ HNO \xrightarrow{18} N_2O + H_2O$$

$$C_2H_5 + HNO \xrightarrow{19} C_2H_6 + NO$$

In view of the considerable complexity of the C_2H_6-NO system, this reaction scheme must be regarded as tentative. In order to get some manageable solution to this scheme, reactions 5, 18 and 19 have been omitted in the following steady-state treatment. In the case of reaction 5 this omission is definitely justified, as discussed earlier. For convenience the following abreviations were made:

$C_2H_6 \equiv RH$, $C_2H_5 \equiv R$, $CH_3CHNOH \equiv Ox$, $CH_3CHN \equiv RN$.

The steady-state equations are:

$$\frac{d[CH_3]}{dt} = 2\ k_1\ [RH] - k_2\ [CH_3][RH] + k_{17}\ [Ox][NO] = 0$$

$$\frac{d[R]}{dt} = k_2\ [CH_3][RH] - k_3\ [R] + k_4[H][RH] - k_6[R][NO] - k_7\ [R][NO] + k_{11}[OH][RH] = 0$$

$$\frac{d[H]}{dt} = k_3\ [R] - k_4\ [H][RH] + k_8\ [HNO] = 0$$

$$\frac{d\,[Ox]}{dt} = k_6\,[R][NO] - k_9\,[Ox][NO] - k_{17}[Ox][NO] - k_{16}[Ox] = 0$$

$$\frac{d\,[HNO]}{dt} = k_7\,[R][NO] - k_8\,[HNO] + k_{15}[RN][NO] = 0$$

$$\frac{d\,[HNO_2]}{dt} = k_9\,[Ox][NO] - k_{10}\,[HNO_2] = 0$$

$$\frac{d\,[OH]}{dt} = k_{10}\,[HNO_2] - k_{11}\,[OH][RH] = 0$$

$$\frac{d\,[RN]}{dt} = k_9\,[Ox][NO] - 2\,k_{12}\,[RN]^2 - k_{13}[RN][NO] - k_{15}[RN][NO] - 2\,k_{14}[RN]^2 = 0$$

Since rates of initiation and termination are equal we have

$$2\,k_1\,[RH] = k_{16}\,[Ox]$$

This gives immediately:

$$\text{(A)}\quad v_{CH_4} = 2\,k_1\,[RH] + \frac{2\,k_1\,k_{17}}{k_{16}}\,[RH][NO].$$

$$\text{(B)}\quad v_{H_2O} = \frac{2\,k_1\,k_9}{k_{16}}\,[RH][NO].$$

Also $[R] = \frac{2\,k_1}{k_6 k_{16}}\,[RH]\left(k_9 + k_{17} + k_{16}\,/\,[NO]\right)$.

and since $v_{15} \ll k_8\,[HNO]$,

$$k_8\,[HNO] = k_7[R][NO] = \frac{2\,k_1 k_7}{k_6\,k_{16}}\,(k_9 + k_{17} + k_{16}/[NO])[RH][NO]$$

Hence,

$$\begin{aligned} v_{H_2} &= k_5[R] + k_8[HNO] \\ &= \frac{2\,k_1 k_5}{k_6\,k_{16}}\,(k_9 + k_{17} + k_{16}/[NO])\,[RH] \\ &\quad + \frac{2\,k_1\,k_7}{k_6\,k_{16}}\,(k_9 + k_{17} + k_{16}/[NO])\,[RH][NO] \end{aligned}$$

or (C) $$v_{H_2} = \frac{2\ k_1 k_3}{k_6} \frac{[RH]}{[NO]} + \left[\frac{2\ k_1}{k_6 k_{16}} (k_9 + k_{17}) k_3 + \frac{2\ k_1 k_7}{k_6}\right] [RH] + \frac{2\ k_1}{k_6 k_{16}} (k_9 + k_{17})\ k_7\ [RH][NO].$$

Further, $v_{C_2H_4} = k_3\ [R] + k_7\ [R][NO] + 2 k_{12} [RN]^2 + k_{13}\ [RN][NO]$.

Since to a very good approximation

$$2\ k_{12}\ [RN]^2 + k_{13}\ [RN][NO] = k_9\ [Ox][NO]$$

and $$k_3 [R] + k_7\ [R][NO] = v_{H_2}$$

(D) $$v_{C_2H_4} = \frac{2\ k_1 k_3}{k_6}\ \frac{[RH]}{[NO]} + \left[\frac{2\ k_1}{k_6 k_{16}} (k_9 + k_{17})\ k_3 + \frac{2\ k_1 k_7}{k_6}\right] [RH] + \left[\frac{2\ k_1}{k_6 k_{16}} (k_9 + k_{17}) k_7 + \frac{2\ k_1 k_9}{k_{16}}\right] [RH]\ [NO]$$

To obtain some approximate expressions for the rates of formation of nitrogen, nitrous oxide and acetonitrile one can assume

$$k_9\ [Ox][NO] \cong 2\ k_{12}\ [RN]^2\ .$$

This is a good approximation at low and intermediate nitric oxide pressures. At very high NO pressures the term $k_{13}[RN]\ [NO]$ becomes important, and then the approximation is not as good.

Hence, $$\frac{2\ k_1 k_9}{k_{16}}\ [RH][NO] = 2\ k_{12}\ [RN]^2$$

or $$[RN] = \left(\frac{k_1\ k_9}{k_{16} k_{12}}\right)^{1/2}\ [RH]^{1/2}\ [NO]^{1/2}\ .$$

This leads to:

$$\text{(E)} \quad v_{N_2} = \frac{k_1 k_9}{k_{16}} [RH] [NO]$$

$$\text{(F)} \quad v_{N_2O} = k_{13} \left(\frac{k_1 k_9}{k_{12} k_{16}}\right)^{1/2} [RH]^{1/2} [NO]^{3/2}$$

$$\text{(G)} \quad v_{CH_3CN} = k_{14} \left(\frac{k_1 \; k_9}{k_{12} k_{16}}\right) [RH] [NO] + k_{15} \left(\frac{k_1 k_9}{k_{12} k_{16}}\right)^{1/2} [RH]^{1/2} [NO]^{3/2}$$

B. Mass Balance

The mass balance with respect to NO requires that

$$[NO] = 2 [N_2O] + 2 [N_2] \quad \text{and} \quad [NO] = [H_2O] + [N_2O]$$

or $[H_2O] = [N_2O] + 2 [N_2]$.

Since from the steady-state equations we have

$$k_9 \; [Ox] [NO] = 2 \; k_{12} \; [RN]^2 + k_{13} \; [RN] [NO]$$

to a very good approximation, the mechanism fulfills the mass balance requirements. Comparing equations (B), (C) and (D) we see that

$$v_{C_2H_4} - v_{H_2} = v_{H_2O} \; .$$

Table 5 shows that at 596°C for 100 mm C_2H_6 and varying NO pressures these relations hold very well within experimental error. The rates are in arbitrary units, and are interpolated from Figure 22. There seems to be a tendency for the v_{H_2O} values to be somewhat higher than $2 \; v_{N_2} + v_{N_2O}$; this might be due to some additional formation of water via reaction 16. The maximum amount of water available from this source would be 3 rate units.

Table 5

Mass balance for varying nitric oxide pressures at 596° C.

$v_{C_2H_4} - v_{H_2}$	$2\,v_{N_2} + v_{N_2O}$	v_{H_2O}	mm NO
8.5 ± 1.8	7.4 ± 0.5	8 ± 0.8	10
13.5 ± 1.8	14 ± 0.5	15.5 ± 1.5	20
26.5 ± 2.1	27.5 ± 0.7	31 ± 2.4	40
41 ± 2.4	42 ± 1.3	46 ± 3	60
69.5 ± 3.3	72 ± 2.5	77 ± 4.5	100
107 ± 5	122 ± 4.3	123 ± 7	160

For 100 mm C_2H_6 and 83.3 mm NO at different temperatures we have the values shown in Table 6. This table shows that throughout the temperature range studied the above relations are fairly well maintained.

C. Orders with Respect to Ethane and Nitric Oxide

Taking into account that k_3 (13, 15) is pressure dependent, and that k_6 (30) might also be somewhat pressure dependent, one can derive the orders n with respect to ethane and nitric oxide for the rate expressions (A) to (G). In Table 7 the experimental orders are compared with those given by the mechanism.

The subscript "m" refers to the orders as given by the rate expressions (A) to (G). The subscript "exptl." refers to the orders as found experimentally (Figures 7 and 8) at 596° C. The orders given in the columns headed by $v^*_{H_2}$ and $v^*_{C_2H_4}$ refer to the regions where the terms that are independent of NO or proportional to NO are the predominant terms in expressions (C) and (D).

The experimental rate curves (Figure 22) suggest that the rate expressions for hydrogen and ethylene are of the form $v = a/[NO] + b + c[NO]$ at constant ethane pressure. Since at very low NO pressures the hydrogen and ethylene curves tend to coincide, and since both curves extrapolate from high NO pressures to approximately the same point on

Table 6

Mass balance at different temperatures.

°C	$\frac{v_{H_2O}}{2\,v_{N_2} + N_2O}$	$\frac{v_{H_2O}}{C_2H_4 - v_{H_2}}$
549.9	0.98	1.12
564.8	1.08	1.04
580.7	0.95	1.16
596.0	1.13	1.14

Table 7

Orders with respect to ethane and nitric oxide for the rates of production of the primary products at 596° C.

Order with respect to	v_{CH_4}	$v^*_{H_2}$	$v^*_{C_2H_4}$	v_{H_2O}	v_{N_2}	v_{N_2O}	v_{CH_3CN}
C_2H_6(m)	1.0	$1<n<1.5$	$1<n<1.5$	1.0	1.0	0.5	$0.5<n<1$
C_2H_6(exptl.)	1.06 ± 0.04	1.40 ± 0.09	0.91 ± 0.06	0.96 ± 0.06	1.01 ± 0.07	0.7 ± 0.2	0.90 ± 0.07
Pratt (80)	1.07 ± 0.05	1.46 ± 0.04	-	-	1.03	-	-
NO(m)	$0<n<1$	$0<n<1$	$0<n<1$	1.0	1.0	1.5	$1<n<1.5$
NO(exptl.)	0.25 ± 0.02	0.25 ± 0.02	0.86 ± 0.06	0.90 ± 0.07	0.85 ± 0.08	1.30 ± 0.05	1.11 ± 0.11
Pratt (86)	-	-	-	-	0.95	-	-

the rate axis, one might expect a and b to be the same for both cases. At high NO pressures the hydrogen and ethylene curves diverge considerably, and hence the two c's should be different. The relative importance of the three terms depends on the pressure of NO for a given pressure of ethane. Since the three terms may have different orders with respect to both ethane and nitric oxide, the experimental over-all orders will be made up of contributions by all terms, and the orders may also be expected not to be the same at all NO pressures. The experimental orders listed in Table 7 show that for hydrogen production the term independent of NO is dominant, whereas for ethylene production the term proportional to NO is the dominant one. The rate curve (Figure 22) for methane production suggests a rate function of the form $v = d + e\,[NO]$. If one subtracts the intercepts from values on the straight-line portions of the rates for ethylene, hydrogen and methane, respectively, one can obtain order plots for the terms proportional to NO. The order plot of this kind for methane is shown in Figure 8 (curve CH_4). Similar plots for ethylene (curve C_2H_4) and hydrogen (curve H_2) are shown in Figure 27. The orders are listed in Table 8. In all these cases the orders with respect to NO are close to unity, which shows that the terms proportional to NO are indeed proportional to the first power of NO.

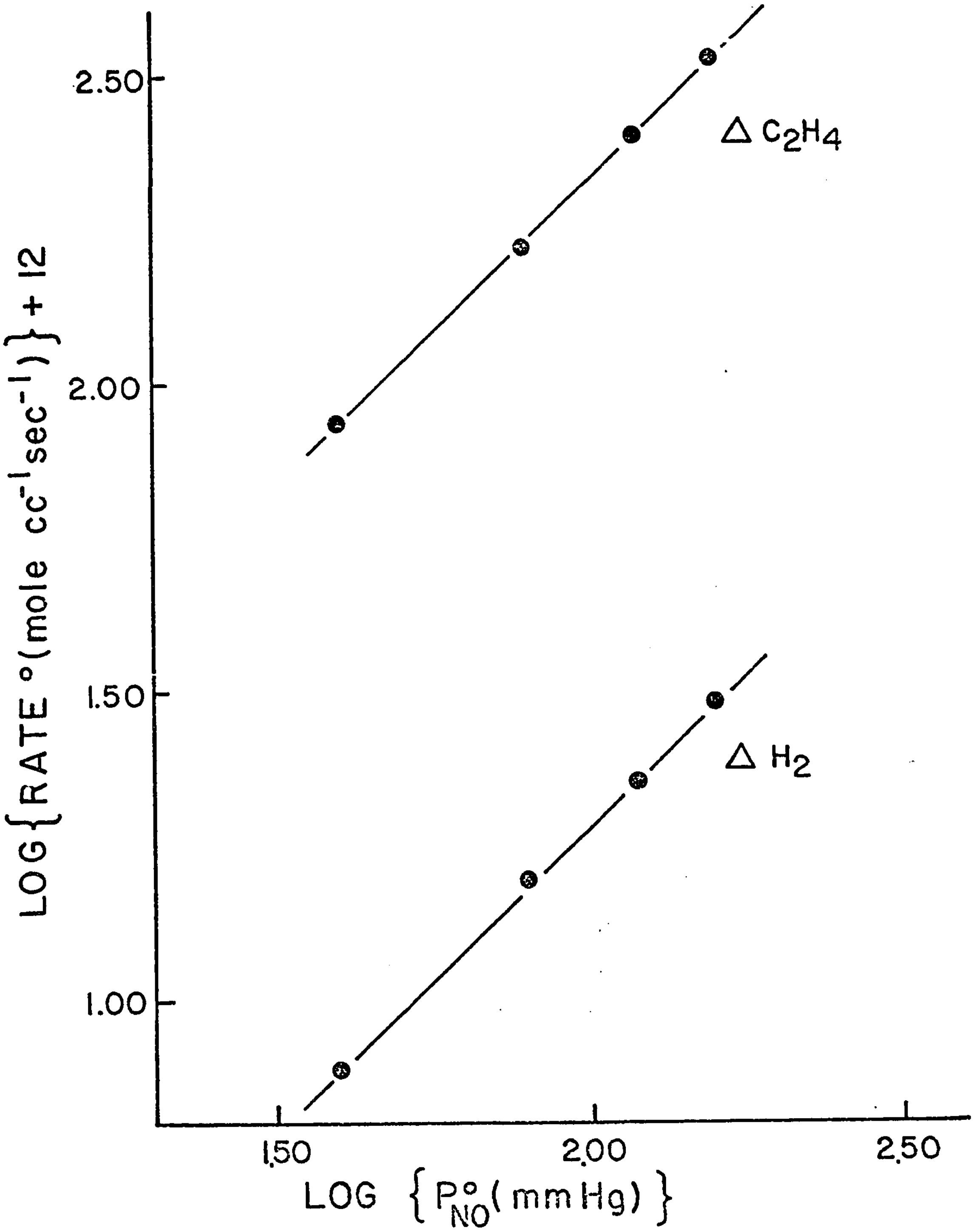
Table 8

Orders with respect to ethane and nitric oxide for those terms in the rate equations of methane, hydrogen and ethylene production which are proportional to nitric oxide pressure.

Orders with respect to	$v_{\Delta CH_4}$	$v_{\Delta H_2}$	$v_{\Delta C_2H_4}$
$C_2H_{6(m)}$	1.0	-	-
$C_2H_{6(exptl.)}$	1.13±0.08	-	-
$NO_{(m)}$	1.0	1.0	1.0
$NO_{(exptl.)}$	0.94±0.05	0.98±0.05	0.98±0.05

Figure 27

Order plots for the rate of production of hydrogen and ethylene for those terms which are proportional to the pressure of NO. Data were obtained from Figure 22.


2.50
2.00
1.50
1.00
1.50
2.00
2.50
LOG {RATE ° (mole cc^{-1} sec^{-1})} + 12
LOG {P^{o}_{NO} (mm Hg)}
Δ C_2H_4
Δ H_2

Tables 7 and 8 show that the experimental orders fall within the limits predicted by the mechanism.

The experimental orders for methane, nitrogen and hydrogen production were also determined by Pratt (80, 86). The present results are in very good agreement with his (Table 7).

D. Derivation of Rate Constants

The hyperbolic form for the variation of rate of hydrogen or ethylene formation with nitric oxide can be tested by plotting against 1/[NO] the difference between the total rate and the sum of the intercept and the asymptote of Figure 22. In terms of equation (C) this means plotting

$$\frac{(2\ k_1\ k_3)}{k_6}\ \frac{[RH]}{[NO]}\ \text{against } 1/[NO].$$

Such a plot is shown in Figure 28. This confirms the functional form of equations (C) and (D) and that the terms proportional to 1/[NO] are indeed identical. The slope of Figure 28 is equal to $2\ k_1k_3[RH]/k_6$ and, since k_1 and k_3 are known, k_6 can be found. Calculation yields a value of $k_6 = 3.12 \times 10^9$ cc mole^{-1}sec^{-1} at 596° C. This is in good agreement with the value of k_6 found by Pratt (80).

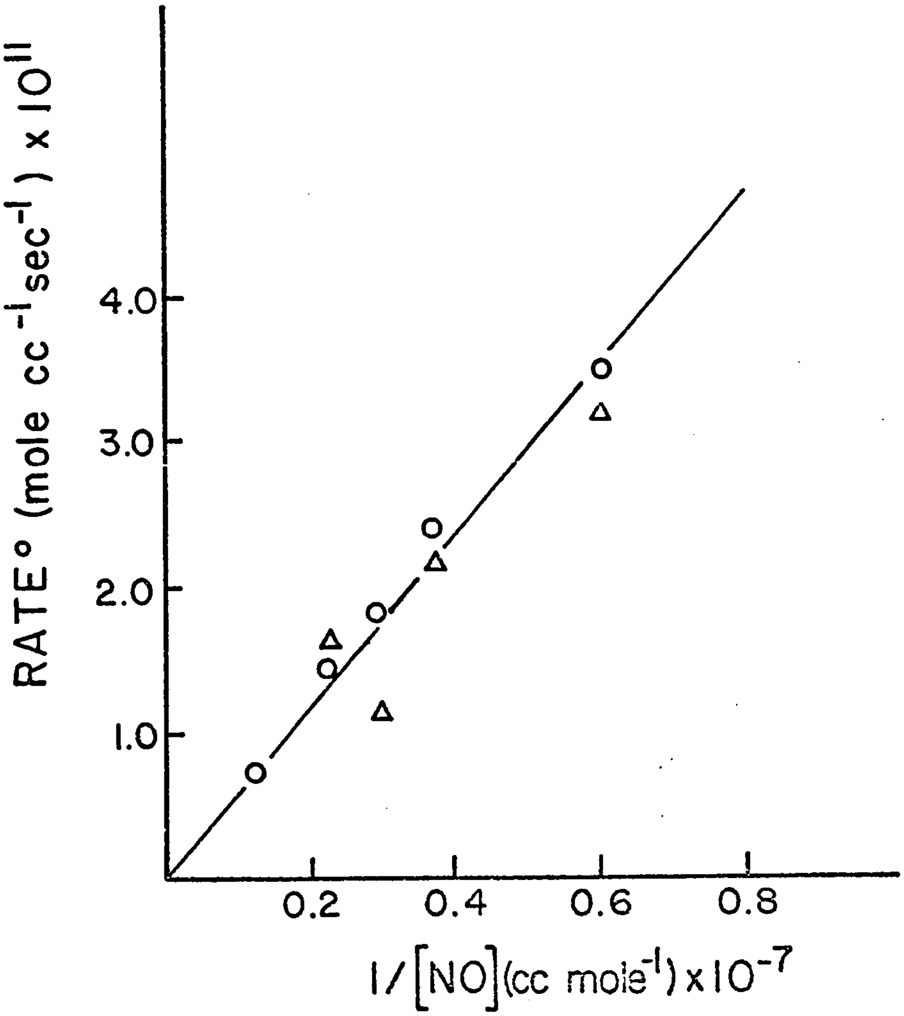
From equations (B) and (C) we see that to a very good approximation the ratio of the term proportional to NO in

Figure 28

Plot of $\frac{2\ k_1 k_3}{k_6}\ \frac{[RH]}{[NO]}$ vs. $\frac{1}{[NO]}$ for 596° C

o rate of hydrogen production

Δ rate of ethylene production


RATE° (mole $cc^{-1} sec^{-1}$) x 10^{11}
4.0
3.0
2.0
1.0
0.2
0.4
0.6
0.8
1/[NO](cc $mole^{-1}$) x 10^{-7}

equation (C) and equation (B) is equal to k_7/k_6. This ratio can be found from Figure 22. From the slopes of the rate curves for hydrogen and water (Figure 22) one calculates $k_7/k_6 = 0.087$ at 596° C. Using the value of k_6 calculated above we find $k_7 = 2.72 \times 10^8$ cc $\text{mole}^{-1}\text{sec}^{-1}$ at 596° C. Since

$$v_{H_2O} = \frac{2\ k_1 k_9}{k_{16}} [RH] [NO],$$

one can also calculate k_9/k_{16}. From the slope of the rate curve for water (Figure 22) and the known k_1 one finds $k_9/k_{16} = 1.41 \times 10^7$ cc mole^{-1}. Similarly, from the slope of the rate curve for methane (Figure 22) one finds $k_{17}/k_{16} = 3.98 \times 10^5$ cc mole^{-1}.

According to the mechanism

$$v_{N_2O} = k_{13}\ [RN] [NO]$$

and

$$v_{N_2} = k_{12}\ [RN]^2$$

and therefore

$$\frac{v_{N_2O}}{v_{N_2}^{\ 1/2}} = \frac{k_{13}}{k_{12}^{\ 1/2}} [NO].$$

Hence, a plot of $v_{N_2O}/v_{N_2}^{\ 1/2}$ vs. $[NO]$ should be a straight line going through the origin. Such a plot is shown in Figure 29. The points at low nitric oxide concentrations deviate a little upward from the line. This might be due to the influence of at least one other minor reaction producing N_2O which has a lower order with respect to NO. The

Figure 29

Plot of $\frac{v_{N_2O}}{v_{N_2}^{1/2}}$ vs. [NO]

Data were obtained at 596° C.

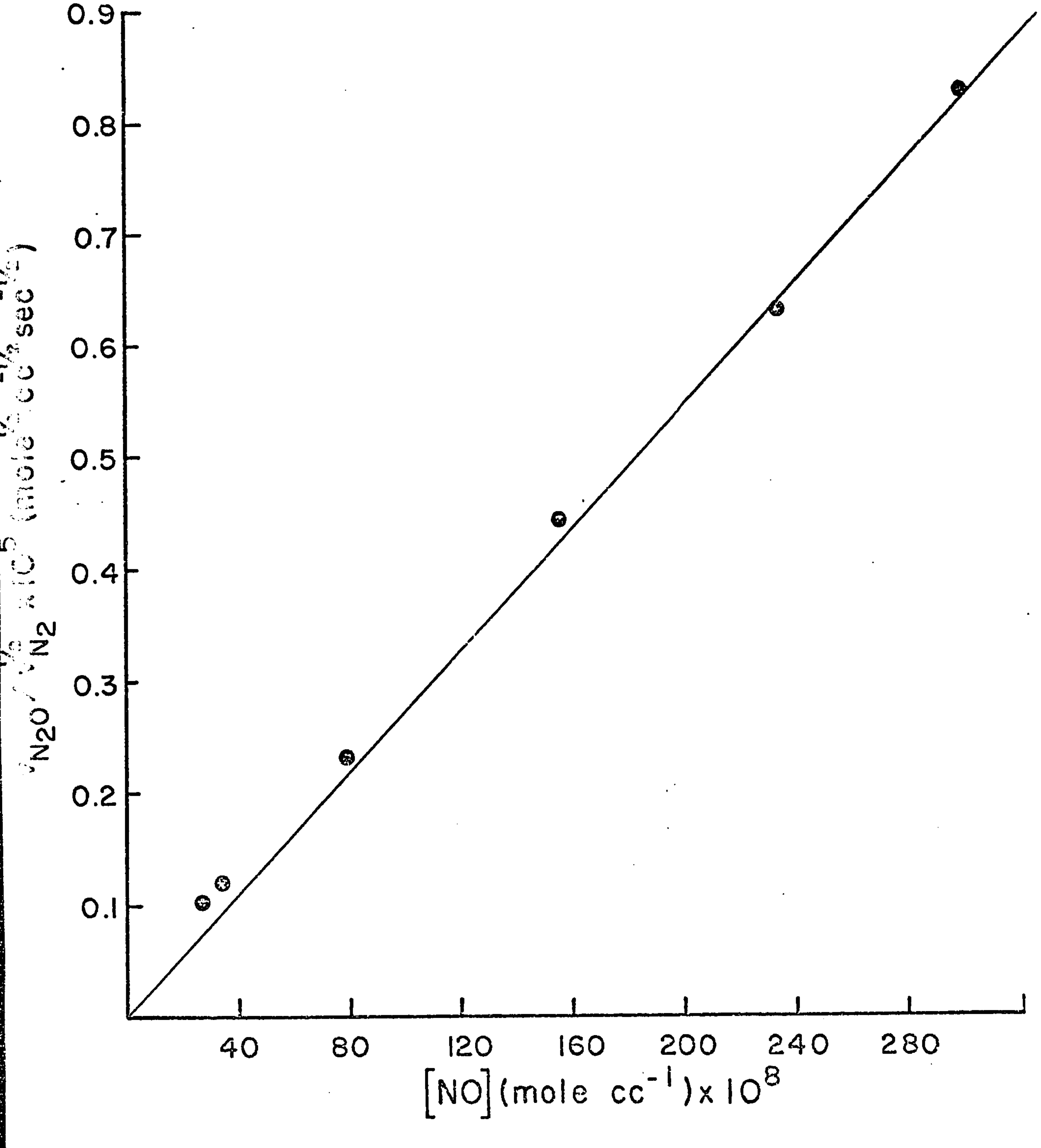

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$r_{N_2O}/r_{N_2}^{1/2} \times 10^5$ (mole$^{1/2}$ cc$^{-1/2}$ sec$^{-1/2}$)
40
80
120
160
200
240
280
[NO] (mole cc^{-1}) x 10^8

Figure 30

Plot of $\frac{v_{CH_3CN}}{v_{N_2}}$ vs. $[NO]^{1/2}$

Data were obtained at 596° C.

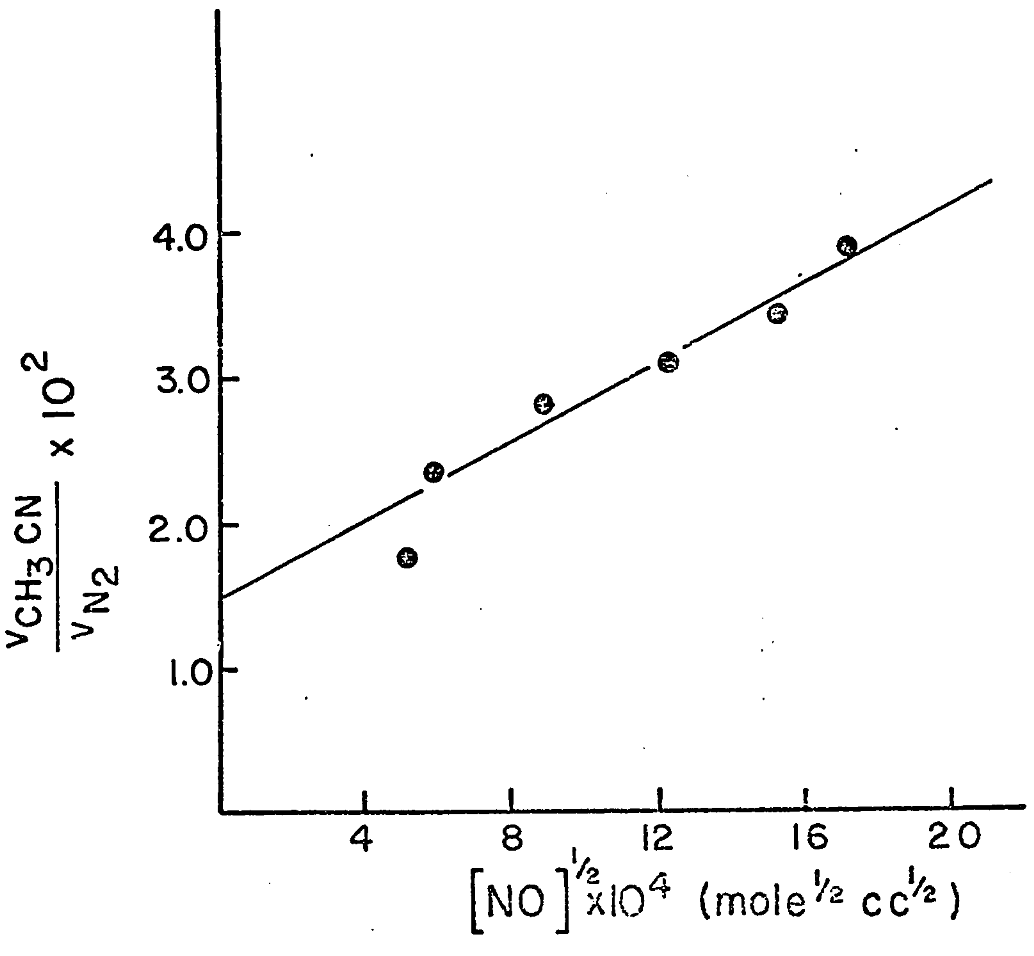

$\frac{v_{CH_3CN}}{v_{N_2}} \times 10^2$
4.0
3.0
2.0
1.0
4
8
12
16
20
$[NO]^{1/2} \times 10^4$ (mole$^{1/2}$ cc$^{1/2}$)

Table 9

Values of k_6, k_7, k_9/k_{16}, k_{17}/k_{16}, $k_{13}/k_{12}^{1/2}$, $k_{15}/k_{12}^{1/2}$ and k_{12}/k_{14} at 596° C.

k_9	3.12×10^9 cc $\text{mole}^{-1}\text{sec}^{-1}$ 3.8×10^9 cc $\text{mole}^{-1}\text{sec}^{-1}$ (Pratt,30)
k_7	2.72×10^8 cc $\text{mole}^{-1}\text{sec}^{-1}$
k_9/k_{16}	1.41×10^7 cc mole^{-1}
k_{17}/k_{16}	3.98×10^5 cc mole^{-1}
$k_{13}/k_{12}^{1/2}$	2.74 $\text{cc}^{1/2}$ $\text{mole}^{-1/2}\text{sec}^{-1/2}$
$k_{15}/k_{12}^{1/2}$	$1.01 \times 10^{-1}\text{cc}^{1/2}$ $\text{mole}^{-1/2}\text{sec}^{-1/2}$
k_{12}/k_{14}	65

were available for several temperatures, one could find accurate activation energies or differences of activation energies for the constants or ratios of constants listed in Table 9. This would make it possible to test the proposed mechanism further.

E. Activation Energies

Activation energies were determined for two different mixtures, namely for a 15.7 % and a 45.5 % mixture. It was found that the activation energies depend on the concentration of NO except those determining the rate of formation of nitrogen and water. The activation energies for these products were constant within experimental error. In the other cases the activation energies decreased with increasing NO concentration. The experimental activation energies are summarized in Table 10. The variation of the activation energies with NO concentration supports the idea that the rate functions are composed of several terms, the relative importance of which depends on the concentration of nitric oxide. The experimental energies will then lie between the limits of the activation energies set by the individual rate terms. Activation energies have been reported by Pratt (30) for the formation of hydrogen and methane for a 16.7 % mixture. These results can be compared with the 15.7 % mixture of this work. The

Table 10

Activation energies for the rate of formation of all primary products for two different C_2H_5-NO mixtures.

Activation energy for production of	15.7 % mixture	45.5 % mixture
C_2H_4	66 ± 2	59 ± 2
H_2	106 ± 3	95 ± 3
CH_4	74 ± 3	68 ± 3
H_2O	56 ± 6	54 ± 6
N_2O	67 ± 3	47 ± 3
N_2	48 ± 3	49 ± 3
CH_3CN	55 ± 6	35 ± 6

activation energy for hydrogen was given as 102 ± 5 kcal mole^{-1}; this is close to the present result. The activation energy for methane, given as 87 ± 4 kcal mole^{-1}, seems a little high, since it is the same as that of the uninhibited reaction and does not reflect the second source of methane with its lower activation energy. An activation energy for nitrogen production was also published (36); its value was given as 62 ± 5 kcal mole^{-1}. Again, this is higher than the value found in the present work.

Of those rate constants appearing in the rate expressions (A) to (G), only k_1 (13, 14, 15) and k_3 (87, 76, 88, 39) have known Arrhenius parameters. In the pressure range used in this work E_1 will be close to the high-pressure value of 36 kcal mole^{-1}, whereas E_3 will be somewhat lower than its high-pressure value, possibly $E_3 = 35$ kcal mole^{-1} (37).

From equation (B) we see that

$$E_{H_2O} = E_1 + E_9 - E_{16} .$$

Hence $$E_9 - E_{16} = 55 - 86 = -31 \pm 6 \text{ kcal mole}^{-1}.$$

As will be shown later $E_{17} - E_{16} = -27$ kcal mole^{-1} and $E_7 = 20$ kcal mole^{-1}; then the rate terms for equation (C) have the following values:

$E_1 + E_3 - E_6 = 121$ kcal mole^{-1}, if $E_6 = 0$

$E_1 + E_9 - E_{16} - E_6 + E_3 = 90$ kcal mole^{-1}

$E_1 + E_{17} - E_{16} - E_6 + E_3 = 121 + E_{17} - E_{16} = 94$ kcal mole^{-1}

$E_1 + E_7 - E_6 = 86 + E_7 = 106$ kcal mole^{-1}

$E_1 + E_9 - E_{16} - E_6 + E_7 = 55 + E_7 = 75$ kcal mole^{-1}

$E_1 + E_{17} - E_{16} - E_6 + E_7 = 86 + E_{17} - E_{16} + E_7 = 79$ kcal mole^{-1}

The over-all value should thus be between 121 and 75 kcal mole^{-1}. The experimental values are 106 and 95 kcal mole^{-1}.

For equation (D) we have the same terms plus one additional one:

$$E_1 + E_9 - E_{16} = 55 \text{ kcal mole}^{-1}.$$

Hence, the over-all value should be between 121 and 55 kcal mole^{-1}. The experimental values are 66 and 59 kcal mole^{-1}.

According to equations (B) and (E) the activation energies for water and nitrogen should be approximately the same. This is found to be the case within experimental error. The activation energies for N_2O and CH_3CN depend strongly on the composition of the reactant mixture. This suggests that the rate functions are made up of at least two terms with different dependence on NO concentration. In the case of nitrous oxide, only one reaction is included in the steady-state treatment of the mechanism. However, although at high NO pressure reaction 13 seems to be the more important one, reaction 18 may also play a role.

Other reactions such as

$$HNO + NO \longrightarrow N_2O + OH \quad (27)$$

might also occur. If reaction 13 is the most important at high NO pressures, then the activation energy should be given approximately by

$$E_{N_2O} = E_{13} - \frac{E_{12}}{2} + \frac{1}{2} (E_1 + E_9 - E_{16}).$$

As will be shown later $E_{13} - \frac{E_{12}}{2}$ is about 23 kcal mole^{-1} and hence

$$E_{N_2O} = 23 + 27 = 50 \text{ kcal mole}^{-1}.$$

E_{N_2O} for a 45.5 % mixture was found to be 47 ± 3 kcal mole^{-1}. This is good agreement in view of the approximate nature of equation (F).

It is more difficult to say how well the experimental activation energy for the production of acetonitrile agrees with that predicted by the mechanism, since not all terms can be evaluated. It is also likely that the rate equation is more complicated than was assumed.

From the data available one cannot - as mentioned earlier - obtain accurate Arrhenius parameters for all the processes proposed for the mechanism. However, approximate estimates of activation energy differences can be obtained for some of them from the available data. The ratio $k_{13}/k_{12}^{1/2}$ is available for several temperatures. If we assume that reaction 13 is the predominant reaction producing N_2O

in the 45.5 % mixture, then $E_{13} - \frac{E_{12}}{2}$ can be calculated to be equal to 22.5 kcal mole^{-1}. This should be an upper limit, since the activation energy for N_2O production at lower NO concentrations indicates that other processes have higher activation energies than reaction 13. The Arrhenius plot is shown in Figure 31. In the same Figure Arrhenius plots are shown of k_9/k_{16} and k_{17}/k_{16}, which yield $E_9 - E_{16} = -25$ kcal mole^{-1} and $E_{17} - E_{16} = -27$ kcal mole^{-1}. To obtain $E_9 - E_{16}$ and $E_{17} - E_{16}$, Arrhenius plots of $v_{H_2O}/ (v^o_{CH_4}[NO])$ and $\left[(v_{CH_4}/ v^o_{CH_4})-1\right]\frac{1}{[NO]}$ were made. The data for $v^o_{CH_4}$, the rate of production of methane in the absence of NO, were not determined directly. Approximate values for $v^o_{CH_4}$ were obtained from extrapolation of v_{CH_4} data - obtained from a 15.7 % and 45.5 % mixture - in a way analogous to that shown in Figure 22 (CH_4 curve). According to equation (B)

$$E_9 - E_{16} = E_{H_2O} - E_1 = -31 \pm 6 \text{ kcal.}$$

Hence, agreement is fairly good.

An estimate of E_7 can be obtained as follows:

$$k_7[R][NO] \doteq k_8\ [HNO]$$

and both $k_3[R]$ and $k_8[HNO]$ can be found from Figure 22. Hence, at 596° C and $[NO] = 1.84 \times 10^{-6}$ mole cc^{-1}

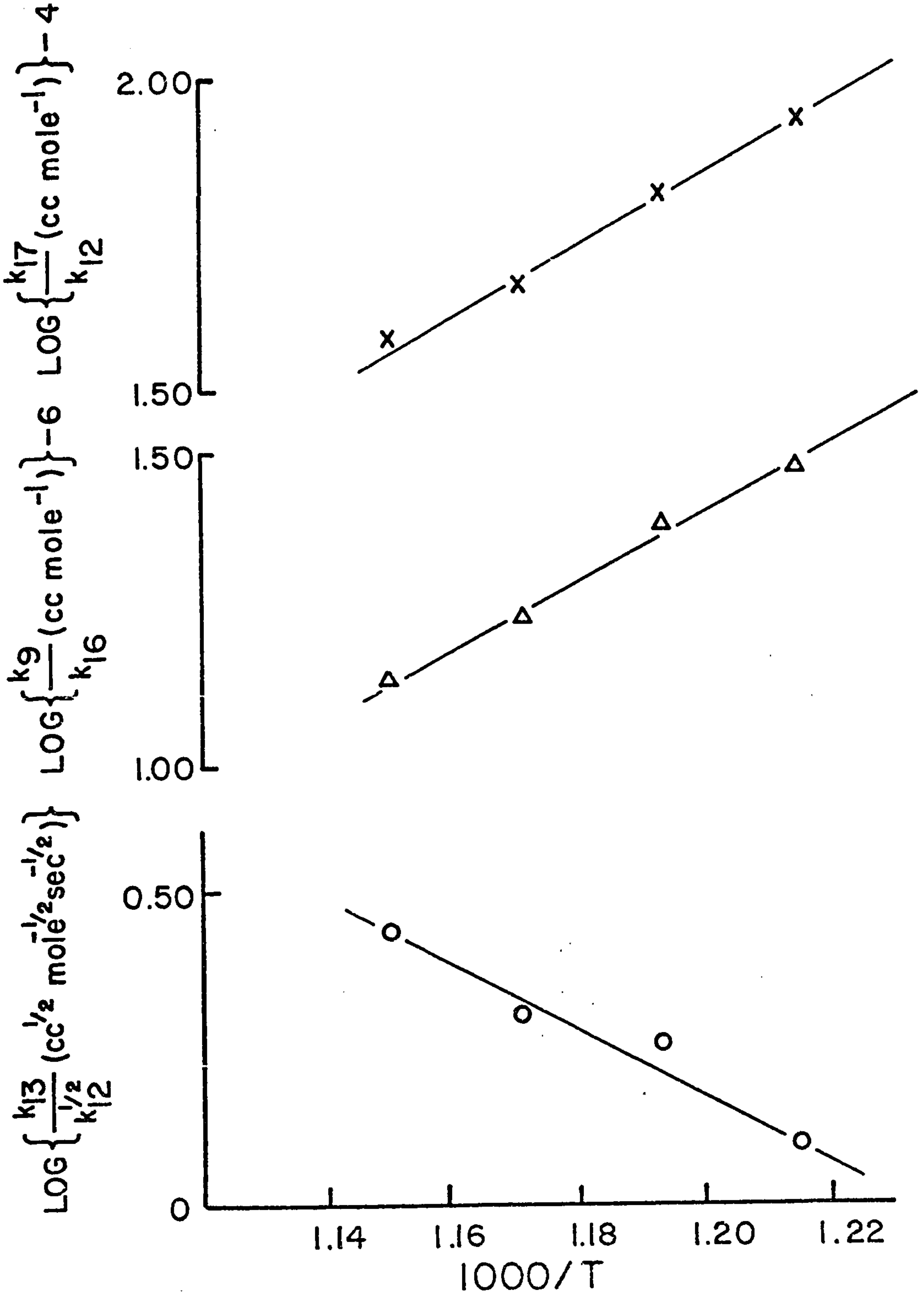
$$\frac{v_3}{v_7} = \frac{k_3\ [R]}{k_7\ [R][NO]} = \frac{4.4 \times 10^{-11} \text{mole cc}^{-1}\text{sec}^{-1}}{2.0 \times 10^{-11} \text{mole cc}^{-1}\text{sec}^{-1}} = 2.2$$

Figure 31

o $\log \dfrac{v_{N_2O}}{v_{N_2}^{1/2}\quad NO} = \log \dfrac{k_{13}}{k_{12}^{1/2}}$ vs. $\dfrac{1}{T}$

Δ $\log \dfrac{v_{H_2O}}{v_{CH_4}^{o}\ [NO]} = \log \dfrac{k_9}{k_{16}}$ vs. $\dfrac{1}{T}$

x $\log \left[\dfrac{v_{CH_4}}{v_{CH_4}^{o}} - 1\right] \dfrac{1}{[NO]} = \log \dfrac{k_{17}}{k_{16}}$ vs. $\dfrac{1}{T}$



$\mathrm{LOG}\left\{\frac{k_{17}}{k_{12}}(\mathrm{cc\ mole^{-1}})\right\}-4$
2.00
1.50
$\mathrm{LOG}\left\{\frac{k_{9}}{k_{16}}(\mathrm{cc\ mole^{-1}})\right\}-6$
1.50
1.00
$\mathrm{LOG}\left\{\frac{k_{13}}{k_{12}^{1/2}}(\mathrm{cc^{1/2}\ mole^{-1/2}sec^{-1/2}})\right\}$
0.50
0
1.14
1.16
1.18
1.20
1.22
1000/T

Now k_3 is known, and if we assume 10^{14} cc mole^{-1}sec^{-1} as the frequency factor of k_7, we obtain $E_7 \cong 20$ kcal mole^{-1}.

At this point it is perhaps interesting to compare the present results with those obtained in the past by pressure measurements. In the pyrolysis of pure ethane the rate obtained from pressure measurements, d $(\Delta P)/dt$, is equal to the rate of production of hydrogen. This is, of course, not the case in the presence of NO, when NO is consumed to any appreciable extent. In such a case we have:

$$\underset{\text{at time t}}{P_{\text{total}}} = P^{o}_{NO} + P^{o}_{C_2H_6} + \sum P_{\text{products}} - \underset{\text{at time t,}}{(P_{NO} + P_{C_2H_6})_{\text{consumed}}}$$

where P^{o}_{NO} and $P^{o}_{C_2H_6}$ are the pressures of the reactants at zero contact time. The pressure change ΔP at time t is then given by

$$\Delta P = \underset{\text{at time t}}{P_{\text{total}}} - (P^{o}_{NO} + P^{o}_{C_2H_6}) = \sum P_{\text{products}} - \underset{\text{at time t.}}{(P_{NO} + P_{C_2H_6})_{\text{consumed}}}$$

Hence,

$$\frac{d\Delta P}{dt} = \frac{d}{dt}\sum P_{\text{products}} - \frac{dP_{NO}}{dt} - \frac{dP_{C_2H_6}}{dt}$$

or

$$\frac{d\Delta P}{dt} = v_{C_2H_4} + v_{H_2} + v_{N_2} + v_{N_2O} + v_{H_2O} + v_{CH_4} + v_{CH_3CN} - |-v_{NO}| - |-v_{C_2H_6}| \cdot$$

From the mass balance we have

$$|-v_{NO}| = v_{H_2O} + v_{N_2O}$$

and

$$|-v_{C_2H_6}| = v_{C_2H_4} + \frac{1}{2} v_{CH4} + v_{CH_3CN}$$

and therefore,

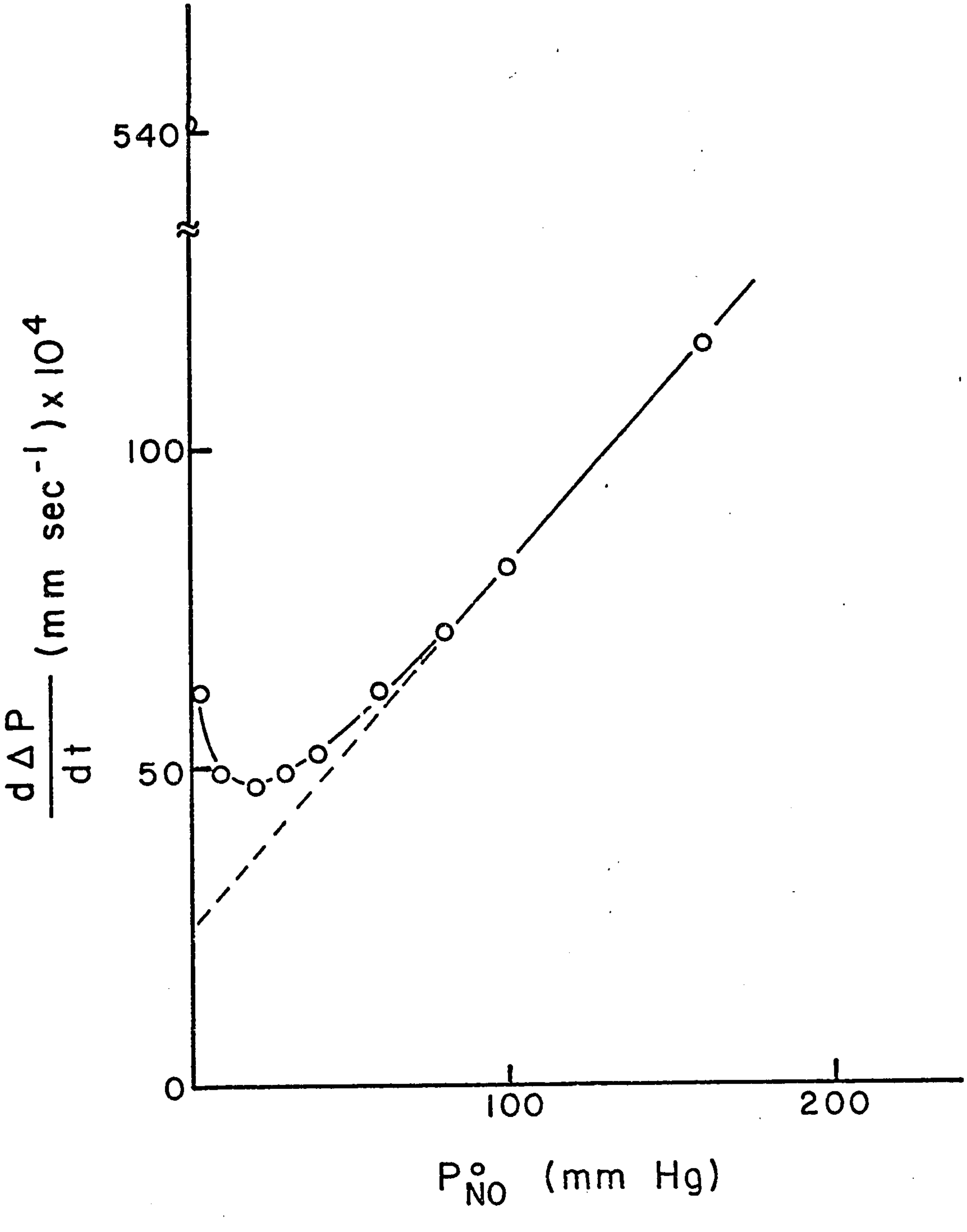
$$\frac{d\Delta P}{dt} = v_{H_2} + v_{N_2} + \frac{1}{2} v_{CH_4}.$$

A plot of $(v_{H_2} + v_{N_2} + \frac{1}{2} v_{CH_4})$ vs. P^o_{NO} should therefore reproduce the well-known inhibition curve. Such a plot is shown in Figure 32. The curve has in fact the expected shape. Arrhenius plots of $(v_{H_2} + v_{N_2} + \frac{1}{2} v_{CH_4})$ are shown in Figure 33. The activation energy for the 15.7 % mixture is 87 kcal $mole^{-1}$; it is of the same order of magnitude as that previously found (52) from pressure measurements in the "maximally inhibited" region. The activation energy for the 45.5 % mixture is 67 kcal $mole^{-1}$; it is considerably lower than the former, as is expected for the "induced" region.

Figure 32

$\frac{d\Delta P}{dt} = (v_{H_2} + v_{N_2} + 1/2\ v_{CH_4})$ vs. P^{o}_{NO}

Data were obtained at 596° C for 100.0 mm C_2H_6 and varying pressures of NO.



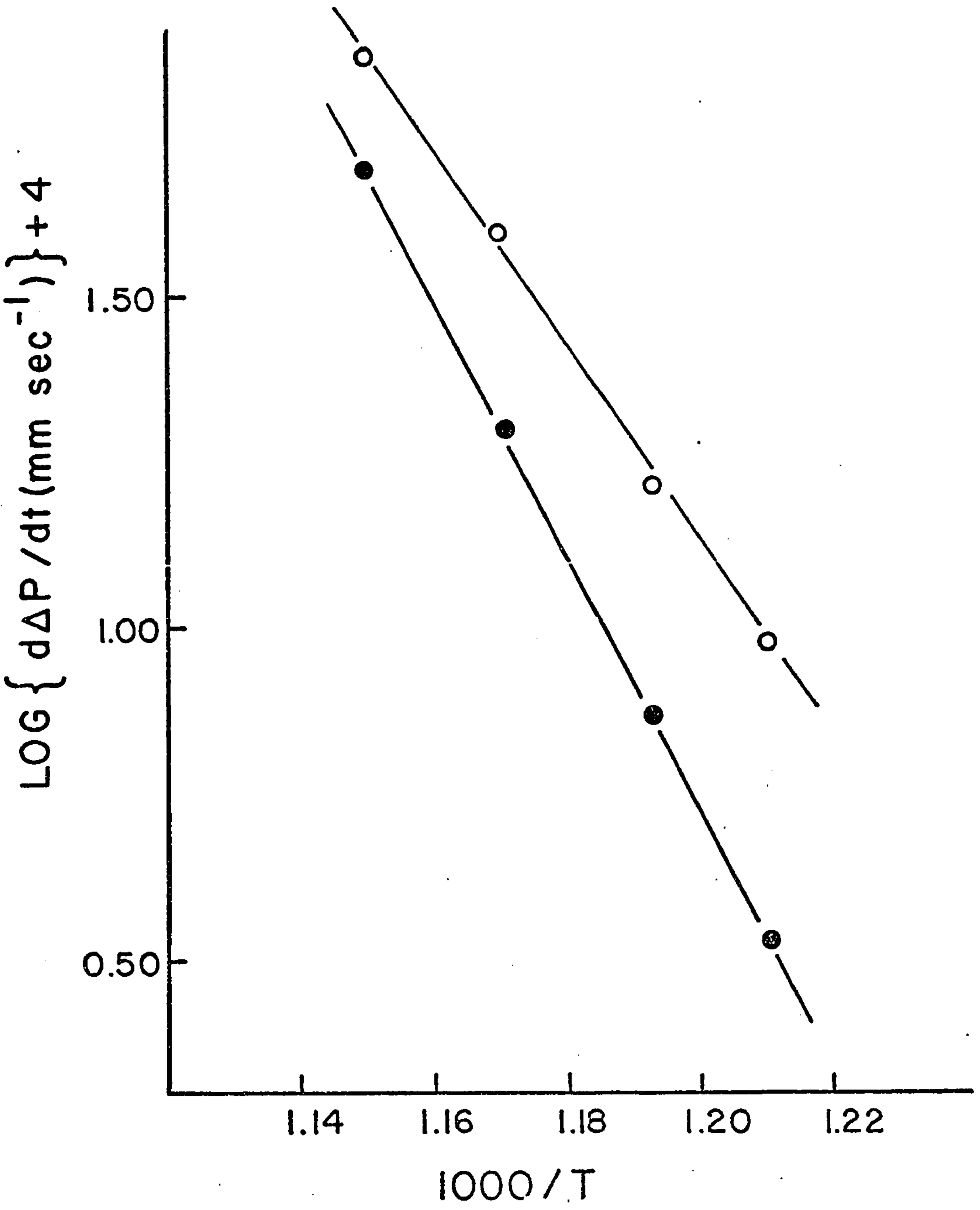
540
100
50
0
100
200
$\frac{d\Delta P}{dt}$ (mm sec^{-1}) x 10^4
P°_{NO} (mm Hg)

Figure 33

$\log \frac{d\,\Delta P}{dt} = \log\,(v_{H_2} + v_{N_2} + 1/2\ v_{CH_4})$ vs. $\frac{1}{T}$

● data for 15.7 % mixture

o data for 45.5 % mixture



LOG {dΔP/dt (mm sec⁻¹)} + 4
1.50
1.00
0.50
1.14
1.16
1.18
1.20
1.22
1000/T

Chapter IV

MECHANISMS OF SECONDARY REACTIONS

Many secondary reactions can be envisaged for the C_2H_6-NO system. Since the main emphasis in this work is on the kinetics of the primary reactions, only a qualitative interpretation is attempted for the secondary reactions observed.

It is known that ethylene is more reactive than ethane and that the presence of ethylene in the pyrolysis of ethane leads to the formation of many secondary products (90, 91). The activation energies for the addition of radicals such as H, CH_3, C_2H_5 to the ethylenic double bond are only a few kcal mole^{-1}. However, abstraction reactions can also occur readily. The resulting radicals may be able to isomerize, abstract from ethane and decompose unimolecularly. It has been shown that these interactions of C_2H_4 with radicals can explain the self-inhibition of the ethane pyrolysis and the secondary production of methane and butane which have been observed in the absence of NO (90, 91). Some of the secondary products which have been discovered previously in the pyrolysis of pure ethane are methane, propylene, n-butane, butene-1, cis- and trans-butene-2, butadiene-1,3, and acetylene (90, 91). A check was made for the C_4-hydrocarbons and all were found also in the presence of NO. However, the induction periods were longer and the amounts produced smaller than those in the absence of NO.

The following reactions can explain the production of the C_4-hydrocarbons in the pyrolysis of pure ethane:

$$C_2H_5 + C_2H_4 \longrightarrow n\text{-}C_4H_9$$

$$n\text{-}C_4H_9 + C_2H_6 \longrightarrow n\text{-}C_4H_{10} + C_2H_5$$

$$n\text{-}C_4H_9 \longrightarrow C_4H_8\text{-}1 + H$$

$$n\text{-}C_4H_9 \longrightarrow sec\text{-}C_4H_9$$

$$sec\text{-}C_4H_9 \longrightarrow cis\text{-}C_4H_8\text{-}2 \text{ and } trans\text{-}C_4H_8\text{-}2$$

$$R + C_2H_4 \longrightarrow RH + C_2H_3, \text{ where } R \equiv H, CH_3, C_2H_5$$

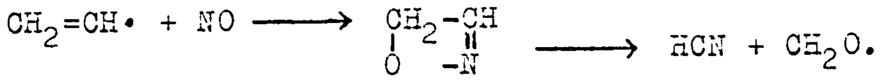
$$C_2H_3 + C_2H_4 \longrightarrow C_4H_7$$

$$C_4H_7 \longrightarrow C_4H_6\text{-}1,3 + H$$

$$C_4H_7 + C_2H_6 \longrightarrow C_4H_8\text{-}1 + C_2H_5$$

In the presence of NO these reactions will still take place, but the products arising from these reactions will occur in smaller quantities, since the NO will scavenge to a large extent the radicals involved. The radicals $n\text{-}C_4H_9$, $sec\text{-}C_4H_9$, C_4H_7 will form oximes with nitric oxide. The oximes in turn will most likely decompose to give rise to a number of additional secondary products. The radical C_2H_3 is known to react differently with NO.

Sherwood and Gunning (92, 93) have shown that vinyl ($C_2H_3\cdot$) and ethynylvinyl ($HC{\equiv}C{-}CH{=}CH\cdot$) radicals react with NO at room temperature to give HCN and aldehydes. Hence, one would expect the C_2H_3 radicals to react as follows:



$$CH_2{=}CH\cdot + NO \longrightarrow \begin{array}{cc} CH_2- & CH \\ | & \| \\ O & -N \end{array} \longrightarrow HCN + CH_2O.$$

HCN is indeed a secondary product; but CH_2O is not found. This is perhaps no surprise, since formaldehyde will decompose readily to yield CO and H_2 at the temperatures involved. Examples of yield-time plots for the C_4-hydrocarbons and HCN are given in Figures 26 and 25, respectively. If the CH_2O arising from the above reaction were the only source of CO, then the induction period for the production of CO should be either the same as that for the production of HCN or even longer; actually, it is much shorter. This means that there is at least a second source of CO. Such a source is the product nitrous oxide. It has been found by Trenwith et al. (94) that nitrous oxide decomposes in the presence of ethane at temperatures well below those where N_2O decomposes by itself. The products of the C_2H_6-N_2O system suggest the reactions:

$$C_2H_5 + N_2O \longrightarrow C_2H_5O + N_2$$

$$C_2H_5O \longrightarrow CH_3 + CH_2O$$

$$C_2H_5O \longrightarrow CH_3C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$$

$$CH_2O \longrightarrow H_2 + CO$$

$$CH_3C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H} \longrightarrow CH_4 + CO$$

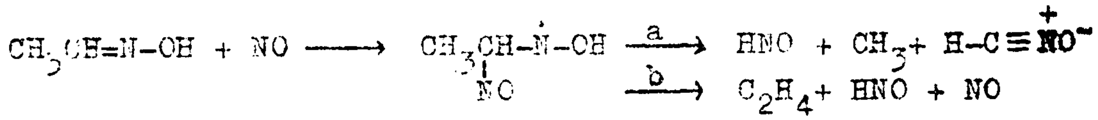
Small amounts of acetaldehyde are indeed found in this work as secondary product (Figure 25). Also the decrease in rate of production of N_2O as the reaction proceeds (Figure 13) is in line with this argument. CH_3 does not react with N_2O in a similar way.

There is no doubt that other secondary reactions can be suggested for a system as complex as the C_2H_6-NO system. However, at this time there is no point in making more detailed proposals and one has to wait till more experimental data are available.

Chapter V

CONCLUSION

The mechanism proposed to explain the C_2H_5-NO system is no doubt simpler than the truth, and one can probably devise different ones to explain the experimental facts. However, it seems hard to avoid the assumption that acetaldoxime is a highly important intermediate which provides an alternative route for the $\mu \longrightarrow \beta$ transition of the ethyl radical, in line with the Norrish-Pratt proposals. Nitroxyl might be more important than the mechanism suggests, since reactions such as



$$CH_3CH{=}N{-}OH + NO \longrightarrow \underset{\displaystyle NO}{CH_3\overset{|}{C}H}{-}\dot{N}{-}OH \begin{array}{l} \xrightarrow{a} HNO + CH_3 + H{-}C{\equiv}\overset{+}{N}O^{-} \\ \xrightarrow{b} C_2H_4 + HNO + NO \end{array}$$

$$C_2H_6 + NO \longrightarrow HNO + C_2H_5$$

$$HNO + NO \longrightarrow OH + N_2O$$

can be envisaged. The first of these reactions along path 'b' - when used instead of reaction 7 (p.84) - fits the kinetics just as well. The same reaction along path 'a' might be a source of CH_3 radicals and would correspond to reaction 17 (p.85). The fulminic acid produced simultaneously would rapidly react further. Another reaction yielding the same products would be

$$CH_3{-}CH{=}NOH + NO \longrightarrow HNO + CH_3{-}CH{=}N{-}O\cdot \longrightarrow CH_3 + H{-}C{\equiv}\overset{+}{N}{-}O^{-}$$

Another matter is the participation of heterogeneous reactions. As was mentioned in Chapter I, and as has been discussed in greater detail elsewhere (24), the participation of heterogeneous processes in the pyrolyses of hydrocarbons in the presence and absence of inhibitors has been a subject of great controversy. No attempt was made to check whether the formation of any of the products was dependent on the surface/volume ratio. Such dependence, however, may well exist. Notwithstanding these reservations the proposed mechanism gives a good interpretation of all the experimental results.

The results and the subsequent discussion clearly show that the addition of nitric oxide to ethane greatly complicates the pyrolysis of the latter. Such complications can also be expected for other hydrocarbon pyrolyses, at least in such cases where the ethyl radical is an important intermediate. The stoichiometry of the combined decomposition of ethane and nitric oxide varies, of course, with the experimental conditions; but under all conditions the NO has to be regarded as a reactant. For a 45.5 % mixture at 596° C e.g., the reaction stoichiometry is given approximately by

$$4\ C_2H_6 + 4\ NO = 4\ C_2H_4 + H_2 + 3\ H_2O + N_2 + 0.5\ N_2O.$$

As mentioned in Chapter I, olefins have also been used in inhibition studies of hydrocarbon pyrolyses. In the case of the C_4H_{10}-C_3H_6 system some detailed product analysis has been made (70). Although the influence of the addition of propylene on the product distribution in the butane pyrolysis is not as drastic as that which NO has on the product distribution in the ethane pyrolysis, it was clearly found that the initial product distribution became more complicated in the presence of C_3H_6, and that the pyrolysis of the C_4H_{10}-C_3H_6 system can be regarded as a co-pyrolysis involving mutual sensitization. Thus it seems that addition of inhibitors does not simplify but complicate organic pyrolyses, and that every system has to be considered on its own merits.

CLAIMS TO ORIGINAL RESEARCH

1. Nitric oxide has been found to decompose rapidly in the ethane pyrolysis with a finite initial rate.

2. The formation of the primary products ethylene, hydrogen, methane, nitrogen, water, nitrous oxide and acetonitrile have been studied in detail.

3. Orders of the rates of formation with respect to ethane and nitric oxide have been determined for all primary products at 596° C.

4. Activation energies for the production of all primary products have been measured in the temperature range 550° to 596° C. The activation energies - except those for the production of nitrogen and water - were found to depend on the composition of the mixture.

5. A mechanism has been proposed which can account for all experimental facts.

6. The following rate parameters have been evaluated for a temperature of 596° C:
k_6, k_7, k_9/k_{16}, k_{17}/k_{16}, $k_{13}/k_{12}^{1/2}$, $k_{15}/k_{12}^{1/2}$, k_{12}/k_{14}.
Estimates of E_9-E_{16}, $E_{17}-E_{16}$, $E_{13}-1/2E_{12}$ and E_7 have been made.

7. Reactions have been proposed to explain the formation of the secondary products observed.

8. It has been shown that rate measurements based on pressure change are related to the rates of formation of hydrogen, nitrogen and methane.

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