THE REACTIONS OF ACTIVE NITROGEN WITH NITRIC OXIDE AND NITROGEN DIOXIDE

by

Gentil J. O. Verbeke

A thesis submitted to the Faculty of Graduate Studies and Research of McGill University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

From the Physical Chemistry Laboratory under the supervision of Dr. C. A. Winkler

McGill University
Montreal, Canada

April, 1958

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the National Research Council of Canada for financial assistance in the form of a Bursary and a Studentship, and to the Scientific Research Bureau of the Province of Quebec for the award of a Scholarship.

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INTRODUCTION

Lewis (1) in 1900 was the first to observe the yellow afterglow resulting from the passage of an electrical discharge through nitrogen and to identify its banded spectrum as that of nitrogen.

In 1911 Strutt, later Lord Rayleigh (2), published the first in a series of papers on the chemical reactions of active nitrogen and the emission spectra associated with active nitrogen and its interaction with other substances. Metallic vapours, he found, were converted to the nitrides whereas various hydrocarbons, saturated, unsaturated and even substituted, yielded hydrogen cyanide with a concurrent emission of the CN spectrum.

For a time considerable controversy existed regarding the influence of impurities in the production of the afterglow. Lewis (3), Warburg (4), Compte (5) and Tiede (6) maintained that small amounts of either oxygen or water vapour were essential to emission. It was finally shown be Strutt and Baker (7) and confirmed by Bonhoeffer and Kaminsky (8) and Herzberg (9), that these impurities achieved their effect by modifying the surface of the glass walls.

The identity of the species responsible for the long-lived afterglow, the excitation of many spectral lines and the

chemical reactivity of active nitrogen was very largely in doubt during the next twenty years. Triatomic nitrogen, ionized nitrogen molecules, metastable molecules and atoms have all been considered at various times.

Trautz (10) proposed N_3 in analogy to ozone. All attempts to freeze this out however failed and no peak at mass 42 was ever found in mass spectrometer studies (11). No evidence for the existence of "nozone" can therefore be said to exist.

Molecular nitrogen ions, suggested by Kaplan (12) and Mitra (13), cannot be reconciled with the fact that removal of charged particles did not affect either the afterglow or the chemical reactivity. Worley (14) was unable to detect the absorption lines of N_2^+ in the afterglow and indeed Mitra himself (15) has changed his views.

The great complexity of the many energy levels available to the nitrogen molecule prevented any ready identification of the different possible metastable states; even the currently accepted value for the dissociation energy was not determined until 1944.

Strutt ascribed the reactivity of the glowing gas to atomic nitrogen. Angerer (16), from a study of the decay of the afterglow intensity concluded that the emission resulted from a bimolecular process. Later work by Koenig and Klinkman (17) and Kneser (18)

confirmed this and suggested that the afterglow decay was second order in the active species and first order in ordinary nitrogen. This evidence appeared to favour the recombination of atoms as the source of the afterglow.

Collisions of the second kind, i.e. ones in which excitation energy is given up during collision, were postulated on theoretical grounds by Klein and Rosseland (10) in 1921. Ample experimental evidence for their occurence was soon found by Franck and Cario (20). This led a number of investigators to propose electronically excited molecules as the active species in nitrogen. Saha and Sur (21) suggested metastable molecules of 8.5 e.v., Birge (22) favoured 11.5 e.v. and Mulliken (23) 10.4 e.v. Willey and Rideal (24), on the basis of calorimetric evidence argued for an energy content of only 2 e.v. At first, Willey attributed the excitation of higher energy spectral lines to cumulative processes and chemiluminescence but later he concluded that the excitation was due to a very small concentration of atoms.

In 1925 Sponer (25) revived interest in atomic nitrogen by drawing an analogy to the experiments of Wood (26) and Bonhoeffer (27) with atomic hydrogen which they found persisted much beyond the discharge tube since the atoms could only recombine in the presence of a third body. This view was supported by Birge (28). Further evidence was obtained by Wrede (29) from the pressure differential across a porous plug.

Cario and Kaplan (30) thought active nitrogen to be a mixture of metastable atoms in the ^2D and ^2P states which, in collisions of the second kind with molecules in the A state could give rise to high vibrational levels of the B state. The energies of the ^2D and ^2P atoms, as determined by Compton and Boyce (31) gave support to this theory since they were of the appropriate value to account for the known populations of the various levels of the B state.

Until this time the dissociation energy of nitrogen was still very uncertain. A number of approximations had been made on the basis of Birge-Sponer extrapolations. These estimates ranged from 11.9 e.v. by Birge and Sponer (32) through 9.1 e.v. by Herzberg (33) and 9.5 e.v. by Birge (34) to 8.4 e.v. by Turner and Samson (35). From sensitized fluorescence Gaviola (36) had determined a value of 9.8 e.v. and in two general critiques Mulliken (37) had advocated 9.5 e.v. in 1929 and 9.1 e.v. in 1932.

The afterglow of active nitrogen consists solely of the first positive bands of N_2 and occurs principally from the $\nu' = 6, 11, 12$ of the $B^3\Pi g$ state to the various levels of the $A^3\Sigma_u^+$ state. The energy of these triplet states relative to the singlet states was unknown until the discovery, in 1934, of the Vegard-Kaplan bands and their definite assignment to the transition $A^3\Sigma_u^+$ to $X^1\Sigma_g^+$ (38, 39).

At this very time however, when the position of the triplet states relative to the ground state was finally established, the spectroscopic climate in respect to the dissociation energy of nitrogen changed. A number of studies on the predissociation of the $C^3\pi_u$ and the $B^3\pi_g$ states by Kaplan (40), Herzberg and Sponer (41), Buttenbender and Herzberg (42) and Van der Ziel (43) led to a value of 7.38 e.v. for the dissociation energy of nitrogen. Acceptance of this value made it clearly impossible to attribute the afterglow to the recombination of ground state nitrogen atoms. This in turn gave support to mechanisms, for generation of the afterglow, that involved collisions of the second kind as proposed by Cario and Kaplan (30), Cario (44) and Oldenberg (45). Meyerott (46) and Nicholls (47) suggested that a metastable $a^1\pi_g$ state might be the main component of active nitrogen.

Gaydon (48), in 1944, proposed the value of 9.764 e.v. for $D(N_2)$ on the basis of a reinterpretation of predissociation data of Van der Ziel. A very complete review of all the evidence may be found in his book on dissociation energies (49). Further evidence for this value has since been reported by Kistiakowsky, Knight and Malin (5), Thomas, Gaydon and Brewer (51), Douglas (52) and Toennies and Greene (53).

Considerable evidence has also been accumulated in the last decade that ground state atoms are the principal active species in active nitrogen.

Jackson and Schiff (11) found a large increase in the mass 14 peak in a mass spectrometer on turning on the discharge. Two appearance potentials of 14.7 and 16.1 e.v. respectively were found for mass 14. The former is almost certainly due to ^4S atoms, the latter was tentatively ascribed to ^1D ions. Reinecke (54), who studied the influence of foreign gases, felt that their effect on the afterglow spectrum could be explained by assuming that $B^3\pi_g$ molecules were formed by the recombination of two atoms in the presence of a third body. Heald and Beringer (55) observed the magnetic resonance spectrum of ground state atoms only in active nitrogen; they could not detect either ^2D or ^2P atoms. From a mass spectrometer study Berkowitz, Chupka and Kistiakowsky (56) concluded that ^4S atoms are the principal component of active nitrogen. They estimated the concentration of metastable molecules to be negligible and identified only one appearance potential at 14.8 e.v.

Gaydon (49) first postulated the approach of two normal nitrogen atoms along a $^5\Sigma$ curve followed by a radiationless transition, in the perturbing field of a third body, to the metastable $B^3\pi_g$ state. This same explanation was favoured by Reinecke (54) to account for the predissociation of the $a^1\pi_g$ state. Radiation from the $^5\Sigma_g^+$ state was detected by Herzfeld and Broida (57) in the products of a discharge through nitrogen frozen out at 4.2°K with

Liquid helium. From the kinetics of the afterglow Berkowitz et al. (56) concluded that the mechanism for the afterglow involved the steps:

$$2\,N\,(^4S) + M \rightleftharpoons N_2\,(^5\Sigma_g^+) + M$$

$$N_2\,(^5\Sigma_g^+) + M \longrightarrow N_2\,(B^3\pi_g) + M$$

Kistiakowsky and Warneck (58) studied the population distributions among the vibrational levels of the B state as a function of temperature and found that the extrapolated position of the 19000 cm^{-1} peak at 0°K coincided with the energy of the postulated $^5\Sigma_g^+$ state.

If only ground state atoms are present in significant amounts in active nitrogen, the number of electronically excited molecular states that need be considered is necessarily reduced to the following low lying states: $w^1\Delta_u$, $a'^1\Sigma_u^-$, $^3\Sigma_u^-$, $^3\Delta_u$, $a^1\pi_g$, $B^3\pi_g$ and $A^3\Sigma_u^+$ (59, 60).

Only estimates are available for the energies of the first four of these. Indeed, it is thought unlikely (60) that the $^3\Sigma_u^-$ and $w^1\Delta_u$ states would even be metastable and the lifetime of the $a'^1\Sigma_u^-$ is not likely to be much greater than 10^{-4} sec. since the transition to the $a^1\pi_g$ is probably not very strongly forbidden. Theoretically possible transitions of the $^3\Delta_u$ to the $B^3\pi_g$ state have not actually been observed. From the correlation rules, the only states to be expected from the recombination of two ^4S atoms are the $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $^5\Sigma_g^+$ and $^7\Sigma$ states (57).

Cario (44) and Oldenberg (45) have suggested that $a^1\pi_g$ molecules might be formed from adjacent levels, especially the 6th.,

of the B state. Lichten (60) however has recently measured a lifetime of 1.7×10^{-4} sec. for $a^1\pi_g$ molecules. This certainly precludes an appreciable concentration of this state under the usual conditions of chemical reactions with active nitrogen. The even shorter radiative lifetime (61) of the B state similarly prevents the accumulation of these molecules.

From the absence of the Vegard-Kaplan bands in absorption spectra, Herzberg (62) estimated a lifetime for the $A^3\Sigma_u^+$ state of the order of 0.1 sec. or more. Muschlitz and Goodman (63) in 1953 reported a free space lifetime of the order of 2×10^{-4} sec. from a molecular beam experiment. Their results have been criticized by Lichten (60) on the basis of the uncertainty in their voltage calibration of the exciting electrons. He identifies the lifetime assigned by them to the A state with that of the slightly higher lying $a^1\pi_g$ state and sets a lower limit of 0.01 sec. to the lifetime of the $A^3\Sigma_u^+$ state.

Evans and Winkler (64) have suggested that molecules in the high vibrational levels of the ground state might be formed by collisional deactivation of molecules in the A state and that these could retain energies of the order of 5 to 6 e.v. over many collisions. This has been confirmed by Schwartz and Hertzfeld (65) and Lukasik and Young (66). The latter report lifetimes for excited vibrational levels of nitrogen of the order of 10^6 collisions.

REACTIONS OF ACTIVE NITROGEN

Since 1945 a continuing study of the reactions of active nitrogen with various compounds, most of them organic, has been in progress in this laboratory. Since only the reaction with ethylene is pertinent to the present study, a brief review will suffice for much of the work done previously.

The saturated hydrocarbons which were investigated include methane, ethane (67, 68), propane (69), cyclopropane (70), n-, iso- and cyclobutane (71, 72) and neo- and cyclopentane (73, 74). The major, and sometimes the only nitrogenous product of these reactions was found to be hydrogen cyanide. Hydrogen was produced in all these reactions and with both methane and ethane evidence was found for hydrogen atom reactions.

The reactions of active nitrogen with unsaturated hydrocarbons (75 - 78) were found, in general, to be faster than those with the corresponding saturated compounds. The reactant, present in lesser amount, was completely consumed. Hydrogen cyanide was the major product but small amounts of cyanogen were also produced. The yield of the latter passed through a maximum when the flow rates of active nitrogen and the olefin were approximately equal.

Methyl, ethyl, vinyl, propyl and isopropyl chlorides (79) were found to react in much the same way as the olefins, i.e. a fast reaction with complete consumption of the reactant not in excess. Hydrogen chloride and hydrogen cyanide were the principal products.

In the majority of the reactions the production of hydrogen cyanide reached a maximal or plateau value at a rather critical flow rate of the hydrocarbon at any one temperature. This plateau was generally found to increase with increase of temperature to a limiting value, above which further increase of temperature had little or no effect.

In a recent paper Evans, Freeman and Winkler (80) have reviewed these reactions and proposed a unified mechanism. Using as an example the reactions of propane, propylene and isopropyl chloride, they suggest that an identical complex of the type

$$CH_3 - \underset{\diagdown\, N\, \diagup}{CH} - CH_2$$

is formed by the interaction of a nitrogen atom and the organic molecule. The authors suggest that the coulomb forces, caused by the interaction of the p-electrons of the carbon atom and the nitrogen atom, allow a very close approach of the latter without surmounting a large potential barrier. The loss of hydrogen or hydrogen chloride is facilitated by the simultaneous delocalization of the orbitals of the C-H and C-Cl bonds. The complex so formed may then decompose with the formation of HCN and a radical

$$(N\ C_3H_6) \rightarrow HCN + C_2H_5$$

and this radical may then split off hydrogen or react further with active nitrogen. Both processes are probably very fast. The rate of formation, the energy content and therefore the lifetime of the complex are dependent on the parent compound. Since the lifetime

has to be sufficient to allow the hydrogen shifts and spin changes involved, its stability will evidently influence the reaction rate.

Forst, Evans and Winkler (81) have suggested that reaction of this complex with a second nitrogen atom may lead to recombination of the nitrogen atoms. The extent of this catalytic recombination is a function of the lifetime of the complex. Since this quantity decreases with rising temperature, this may explain the variation in limiting hydrogen cyanide production with temperature.

One reaction only, of those studied in this laboratory, did not appear to admit of an explanation in terms of nitrogen atoms. Freeman and Winkler (82) found that ammonia, though it diminishes the intensity of the nitrogen afterglow, does not extinguish it. The amount of ammonia destroyed by reaction with active nitrogen, which was apparently temperature independent, amounted to only one sixth of the hydrogen cyanide formed in the reaction with ethylene under conditions of complete reaction with active nitrogen. Nevertheless the reaction seems to be very fast since all the ammonia is destroyed at flow rates below the critical value. The ammonia reaction appears to be truly unique; the analogous phosphorous compound, PH_3, was destroyed at a rate equal to one half the active nitrogen flow rate (83), which suggested the mechanism

$$PH_3 + N \longrightarrow PH_2 + NH$$

$$PH_2 + N \longrightarrow PN + H_2$$

The reaction of active nitrogen with nitric oxide, the subject of the present study, was first investigated by Strutt (84, 85).

He observed a greenish-yellow reaction flame with a continuous spectrum when either NO or NO_2 were introduced into an active nitrogen stream. The appearance of this same flame when ozone reacted with these oxides or when they were fed into a Bunsen Flame, led him to ascribe it to an excited NO_2 molecule. He proposed the mechanism

$$2NO + N \longrightarrow N_2 + NO_2$$

$$NO_2 + NO \xrightarrow[\text{trap}]{\text{cold}} N_2O_3$$

on the basis of which he concluded that the active nitrogen flow rate could be estimated by weighing the amount of N_2O_3 formed. He found the energy liberated by active nitrogen on a copper oxide gauze to be comparable with the heat liberated in the NO active nitrogen reaction (86).

Willey and Rideal (24) reacted NO with active nitrogen and measured the temperature rise when equilibrium was attained in a calorimeter surrounding the reaction vessel. By determining the electrical power necessary to achieve the same temperature rise in the absence of active nitrogen, they obtained a measure of the heat liberated by the reaction. Assuming that the reaction proceeded by the steps:

$$N_2^* + NO \longrightarrow NO^* + N_2$$

$$NO^* + NO \longrightarrow N_2 + O_2$$

$$2NO + O_2 \xrightarrow[\text{trap}]{\text{cold}} 2\,NO_2$$

they used the amount of NO_2 as a measure of the active nitrogen present. They concluded that active nitrogen had an "endothermicity"

of approximately 43 kcal. per mole, i.e. that the excited molecules to which the activity was attributed carried excess energy to the extent of 43 kcal. per mole.

Spealman and Rodebush (87) studied the reaction of NO and NO_2 with both active nitrogen and oxygen and explained their results in terms of the reactions:

$$N + NO \longrightarrow N_2 + O \quad (1)$$

$$N + NO_2 \longrightarrow 2\ NO \quad (2)$$

$$N + NO_2 \longrightarrow N_2 + O_2 \quad (3)$$

$$O + NO \longrightarrow NO_2 \quad (4)$$

$$O + NO_2 \longrightarrow NO + O_2 \quad (5)$$

They estimated their active nitrogen flow rate by measuring the NO produced from NO_2 by reaction (2) and assumed reaction (3) to be slow in comparison. They observed a blue glow at low flow rates of both reactants and the greenish-yellow flame of excited NO_2 at higher flow rates. The green glow disappeared when a large excess of NO_2 was used but did not disappear at any flow rate of NO.

The blue glow emitted when NO or NO_2 are introduced into an excess of active nitrogen is due to the β bands of nitric oxide (88, 89). Kaufman and Kelso (90) made a study of the emission spectrum of a discharge through $N^{14}O$ and $N^{15}O$ and measured the isotope shifts of the band heads. When $N^{15}O$ was introduced into active nitrogen, only

the β bands of $N^{14}O$ were observed. They concluded that the emission must be due to the reactions

$$N + O \xrightarrow{M} NO^{*} \longrightarrow NO + h\nu$$

Kistiakowsky and Volpi (91) recently reported an investigation of the reactions of active nitrogen with NO and NO_2 with a mass spectrometer. Oxygen proved to be the only measurable product of the reaction with NO; other oxides of nitrogen were not found. They proposed the following reaction mechanism

$$N + NO \longrightarrow N_2 + O \qquad (1)$$

$$O + NO \longrightarrow NO_2^{*} \qquad (2)$$

$$NO_2^{*} \longrightarrow NO + O \qquad (3)$$

$$NO_2^{*} + M \longrightarrow NO_2 + M \qquad (4)$$

$$O + NO_2 \longrightarrow NO + O_2 \qquad (5)$$

At a sharply defined flow rate of NO, the effluent gas began to contain unreacted NO, which indicates that all the NO was destroyed as long as active nitrogen was in excess. From an estimate that their mass spectrometer could just have detected 0.02% NO, they determined a lower limit for the rate constant of reaction (1) of 4×10^{11} cc./mole sec.

Nitrous oxide and molecular nitrogen were both found among the products of the NO_2 reaction. When the NO_2 was in excess over active nitrogen both NO and NO_2 were also among the effluent gases; quantitative measurement of NO was not possible however because of the contribution of NO_2 to the mass 30 peak with the electron energy used.

The mole ratio of NO to NO_2 destroyed under the same conditions was unity within 20% as determined from the break in their effluent concentrations. The production of N_2O showed a maximum equal to about 10% of the active nitrogen flow rate when the inflowing NO_2 was approximately one half the active nitrogen flow rate. It slowly rose again, from a minimum at equimolar concentrations of NO_2 and active nitrogen, to a value of approximately 30% of the active nitrogen flow rate when NO_2 was in tenfold excess. The concentration of molecular oxygen in the products rose linearly with NO_2 flow rate to a maximum at equimolar quantitites of NO_2 and active nitrogen and then declined slowly to some 80% of its maximum value. In a number of experiments, where equimolar mixtures of NO and NO_2 were introduced into the reaction vessel, the yield of N_2O was found to be very much reduced especially at low reactant flow rates.

The authors attributed the maximum and minimum in the amount of N_2O produced to a reaction mechanism involving

$$N + NO_2 \longrightarrow N_2O + O \qquad (6)$$

$$O + NO_2 \longrightarrow NO + O_2 \qquad (5)$$

$$N + NO \longrightarrow N_2 + O \qquad (1)$$

If the steady state concentration of atomic nitrogen is assumed to decrease linearly with increasing NO_2 flow rate, a maximum is indeed to be expected. The marked reduction in N_2O formation from mixtures of NO and NO_2 was cited as evidence that reactions (1) and (5) were

faster than (6). The asymptotic rise of N_2O yield at high NO_2 concentrations was attributed to the preponderance of reactions (5) and (6). The following reactions

$$N + NO_2 \longrightarrow N_2 + O_2 \qquad (7)$$

$$N + NO_2 \longrightarrow 2NO \qquad (8)$$

were also invoked, reaction (7) to account for the ratio of O_2/N_2O which was larger than unity and reaction (8) to account for the slow decrease in O_2 yield beyond equimolar nitrogen atom-NO_2 mixtures.

A suggested explanation for the rise in N_2O formation from mixtures of NO and NO_2 reacting with active nitrogen, involved the reaction of vibrationally excited NO molecules according to the mechanism

$$O + NO_2 \longrightarrow NO^* + O_2 \qquad (9)$$

$$NO^* + NO_2 \longrightarrow N_2O + O_2 \qquad (10)$$

Since atomic oxygen is produced in these reactions of active nitrogen, a brief review of the reactions of oxygen atoms with NO and NO_2 would seem to be appropriate.

Indirect measurements of the rate constants of the reaction

$$NO + O + M \longrightarrow NO_2 + M \qquad (1)$$

by Kaufman, Gerri and Bowman (92) and Ford and Endow (93) gave values of 6×10^{15} and 1.8×10^{16} $cc.^2/mole^2$ sec. respectively. Assuming that the light intensity due to the reaction

$$NO + O \longrightarrow NO_2 + h\nu \qquad (2)$$

is proportional to the atomic oxygen concentration, Kaufman (94) has recently determined a value for the rate constant of reaction (1) of 2×10^{16} cc.^{2}/mole^2 sec. with argon or molecular nitrogen as the third body. This is in excellent agreement with the value of 2.15×10^{16} cc.^{2}/mole sec. found from an isothermal calorimetry study (95).

Ford and Endow (93) calculated a rate constant for the reaction

$$O + NO_2 \longrightarrow NO + O_2 \qquad (3)$$

of 2.1×10^{12} cc./mole sec. Kaufman (94) found a lower limit of 10^{11} cc./mole sec. for reaction (3) while Kistiakowsky and Kydd (96) set a lower limit of 10^{12} cc./mole sec.

It follows from these data that, in the pressure range of 1 to 3 mm., where active nitrogen reactions are usually studied, reaction (3) is some 500 times faster than reaction (1). This was experimentally confirmed (97) by mass spectrometer studies; the ratio of NO to NO_2, in the presence of excess oxygen atoms, was found to reach a value between 30 and 200 when either NO or NO_2 were introduced into atomic oxygen.

Kaufman (94) has recently made use of the emission reaction (2), which occurs as long as atomic oxygen is present, to measure its concentration. When an amount of NO_2, equal to the amount of oxygen atoms is added, the latter are presumably all removed by reaction (3) and the abrupt disappearance of the green afterglow indicates the "end point" of

the titration. It has been found however (95) that the oxygen atom concentration, measured by this technique, was only 85% of the value indicated by the heat given up at a silver wire on which the atoms recombined. In addition, reaction (2) appeared to be incompletely suppressed since a certain amount of radiation was still visible when an excess of NO_2 was introduced into the atomic oxygen stream.

THE PRESENT PROBLEM

In previous studies in this laboratory it has frequently been assumed that active nitrogen concentrations could be taken to correspond to the essentially constant (within 10%) limiting amount of hydrogen cyanide produced in the reactions of active nitrogen with both unsubstituted and substituted hydrocarbons at elevated temperature. The constancy of the limiting yields are especially evident with fast reactions such as those of ethylene and methyl chloride. The author has found, for example, that the flowrate of active nitrogen, determined from the hydrogen cyanide yield from these two reactions, was identical within the limits of experimental error.*

Wrede gauge measurements of the concentration of atomic nitrogen (67, 75) were also in good agreement with the values deduced from hydrogen cyanide formation.

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* These data were obtained during work that was preliminary to the investigation reported in this thesis.

On the other hand, the concentration of active nitrogen indicated by the amount of ammonia destroyed proved to be exceptionally low and strongly suggested in fact, that ammonia reacted with only one of two (or more) chemically active species in active nitrogen.

Since earlier work by other investigators (85, 24, 87) had indicated that the extent of the active nitrogen NO reaction might be used as a measure of the concentration of the former, it was decided that the reactions of active nitrogen with oxides of nitrogen should be reinvestigated with the equipment and procedures used in this laboratory in an effort to resolve the apparent discrepancy between the estimates of active nitrogen concentrations based on the hydrocarbon and ammonia reactions.

EXPERIMENTAL

MATERIALS

Nitric oxide was obtained from the Matheson Co. It contained N_2, N_2O, N_2O_3 and NO as impurities. Nitrogen was pumped off while the nitric oxide was kept at liquid nitrogen temperature. N_2O_3 and NO_2 were removed by two distillations from a frozen pentane bath at -130°C. Finally, the nitric oxide was allowed to warm to its melting point and the gas bled off slowly so that the distillation occurred under approximately equilibrium conditions. Infra-red analysis of the product showed it to contain no traces of higher oxides and, from the very intense band at 2240 cm^{-1}, to contain less than 0.3% nitrous oxide.

Nitrogen dioxide was prepared by treating purified nitric oxide with an excess of oxygen distilled from liquid oxygen. When the deep blue colour of N_2O_3 was no longer visible in the condensed material, the excess oxygen was pumped off. Halocarbon stopcock grease, containing no hydrogen, was used in all parts of the system in contact with the nitrogen dioxide. The nitrogen dioxide was normally kept frozen, when not in use, to prevent photochemical decomposition. Frequent checks were made for the presence of N_2O_3 and, whenever necessary, the oxidation was repeated.

Ethylene, 99% pure, was obtained from the Ohio Chemical Co., and further purified by degassing at -196°C, followed by two bulb to bulb distillations from which only the middle fractions were used.

Commercial anhydrous ammonia was obtained from Canadian Industries Ltd., and twice vacuum distilled.

Dry-pumped nitrogen, 99.7% pure, was obtained from Linde Air Products Co. Mass spectrometric analysis confirmed that it contained less than 0.2% oxygen and only a trace of argon. It was passed over copper turnings at 350°C and through a cold trap prior to use.

APPARATUS

The apparatus was essentially similar to that used in previous investigations of active nitrogen reactions in this laboratory.

A line drawing of the apparatus is shown in Figure 1. Nitrogen, from a cylinder, passed through a simple dibutyl phthalate manostat, through a tube containing copper turnings maintained at 350-375°C by a furnace A, through a trap surrounded by liquid nitrogen or a dry-ice acetone mixture and finally through the drawn-out capillary of the flowmeter B. The flow rate through this capillary was determined from the rate of evacuation of a known volume and the flow head measured by the manometer M_1.

From the flowmeter, the nitrogen passed into the ends of the V-shaped discharge tube C, made of 25 mm. tubing with a distance of 52 cm. between the aluminum electrodes, then out through the center,

through 12 cm. of 18 mm. tubing into a 300 cc. spherical reaction vessel which could be surrounded by a furnace and which was provided with a thermocouple well and an inlet for reactant. A second reaction vessel, Figure 2, consisted of 140 cm. of 18 mm. tubing, connected immediately below the center of the discharge tube through a constriction. Into the side of this tube, at different distances downstream, were placed 6 reactant inlets; by a system of stopcocks the reactant could be admitted through any one of these. The entire reaction tube was wrapped with glass tape and nichrome wire, arranged so that the space between any two inlets could be raised to the desired temperature. The inner walls of the discharge tube and both reaction vessels were poisoned with 5% metaphosphoric acid to reduce heterogeneous atom recombination.

Ethylene, ammonia and nitric oxide flow rates were determined from the pressure drop in a calibrated volume over a known time, assuming the gases to be ideal. Different flow rates of reactant were obtained by varying the pressure, measured by manometer M_2, across the capillary flowmeter D. During any one experiment, this flow head was kept constant by leaking in gas from the calibrated volume E through the needle valve F. A ballast volume G in this line provided an adequate time constant for the system.

Because nitrogen dioxide is partially dimerized under the experimental conditions, the calibrated volume was not used in the nitrogen dioxide flow system and the gas was passed directly from a

FIGURE 1

DIAGRAM OF APPARATUS

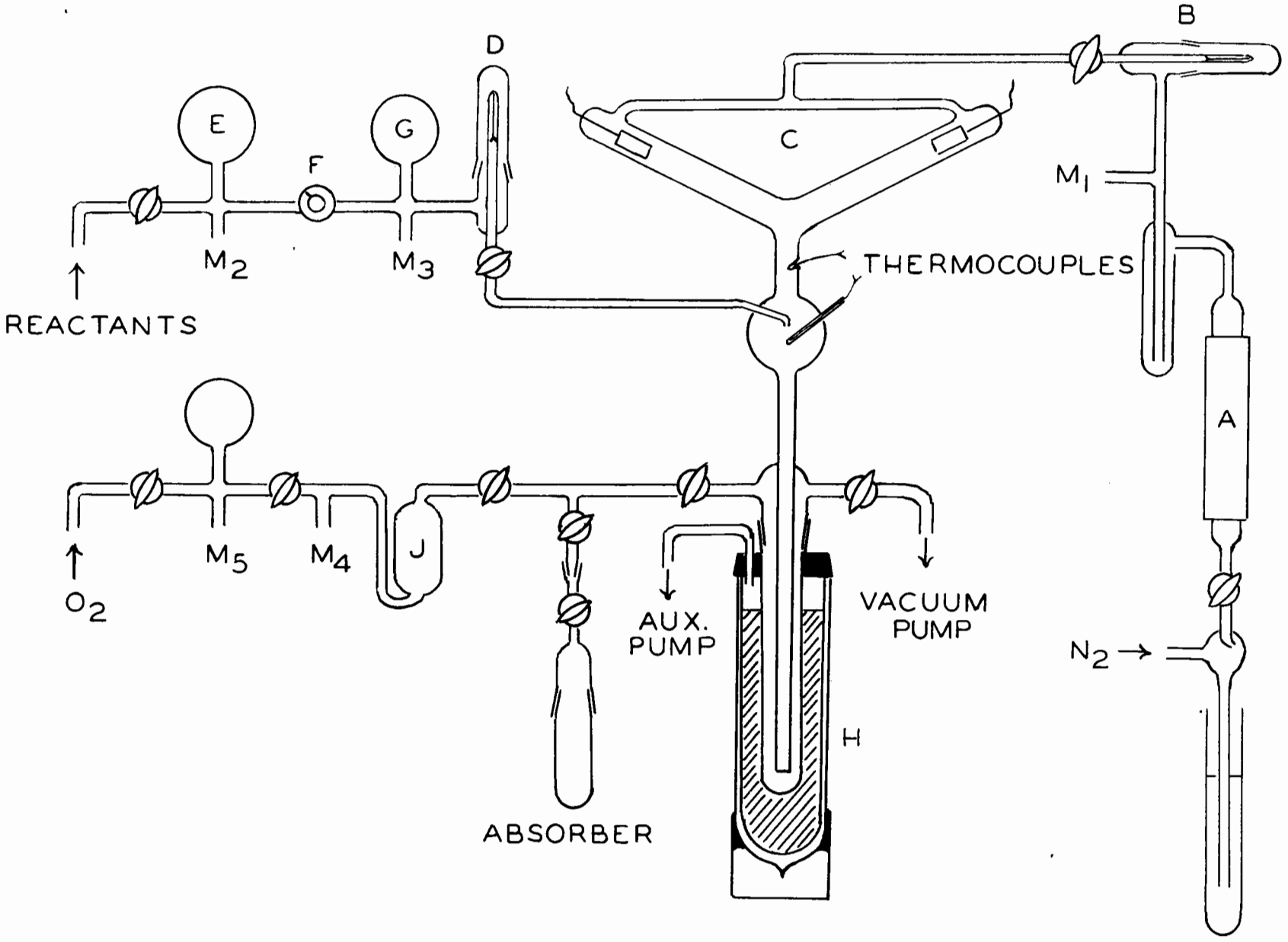
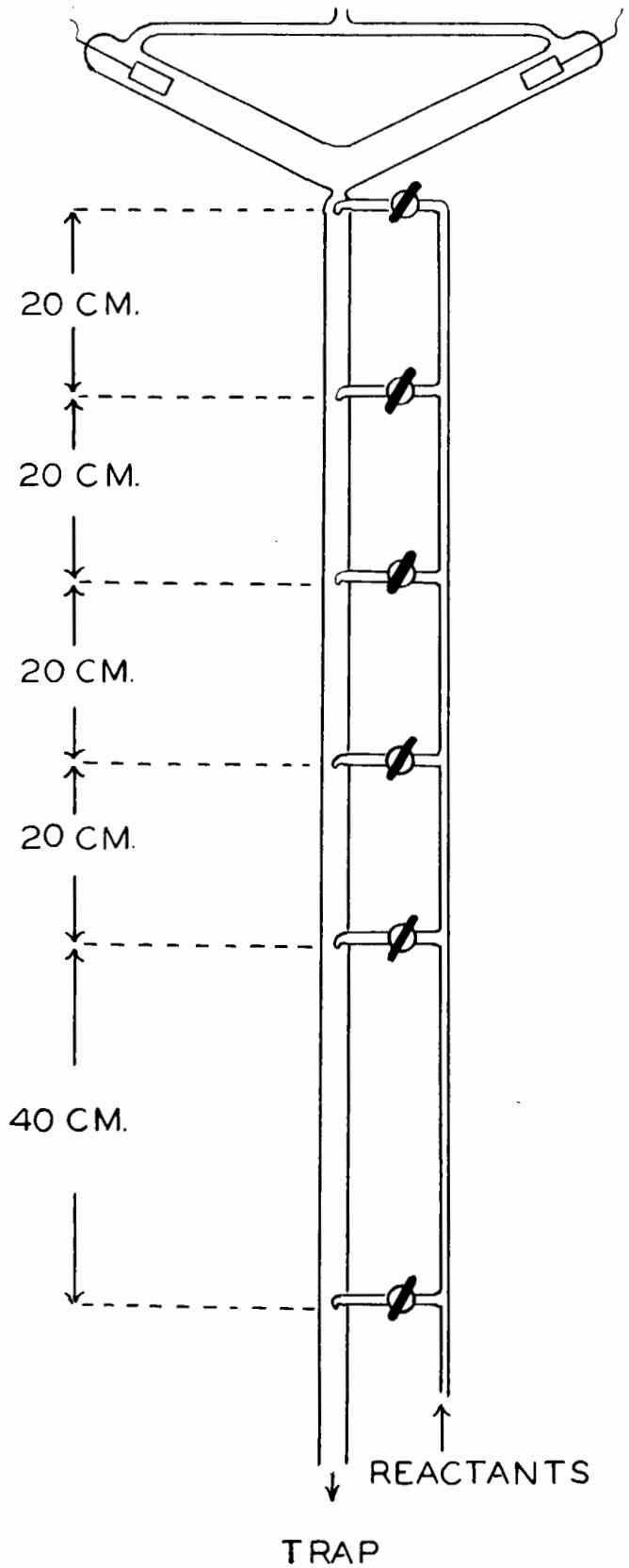

B
D
E
G
F
C
M1
M2
M3
THERMOCOUPLES
REACTANTS
A
M5
M4
J
O2
AUX.
PUMP
VACUUM
PUMP
N2
H
ABSORBER

FIGURE 2

SECOND REACTION VESSEL

(long tube)


20 CM.
20 CM.
20 CM.
20 CM.
40 CM.
REACTANTS
TRAP

large storage bulb, through a needle valve, to the flowmeter. A series of experiments were made without a discharge through the nitrogen, to establish the relation between pressure across the flowmeter and flow rate of nitrogen dioxide. The flow rate proved to be a nearly linear function of pressure, reproducible to within better than 2%.

Before each experiment with nitric oxide or nitrogen dioxide the trap H was surrounded with liquid nitrogen, which was then boiled at reduced pressure until the nitrogen reached its freezing point at -210°C., with an equilibrium vapour pressure of 10 cm. During the twenty minutes of pumping prior to an experiment, an appreciable fraction of the nitrogen froze and only about one third was lost by evaporation. A series of experiments, in the absence of active nitrogen, established that nitric oxide could be trapped quantitatively in this manner. At flow rates where active nitrogen was in excess of either nitric oxide or nitrogen dioxide, ozone formation occurred in the cold trap; when this had been confirmed by an explosion, a small coil, wound from two feet of silver wire, was placed ahead of the trap. Ozone formation was completely eliminated by this device, presumably by catalyzing the recombination of oxygen atoms, without in any other way affecting the behaviour of the system.

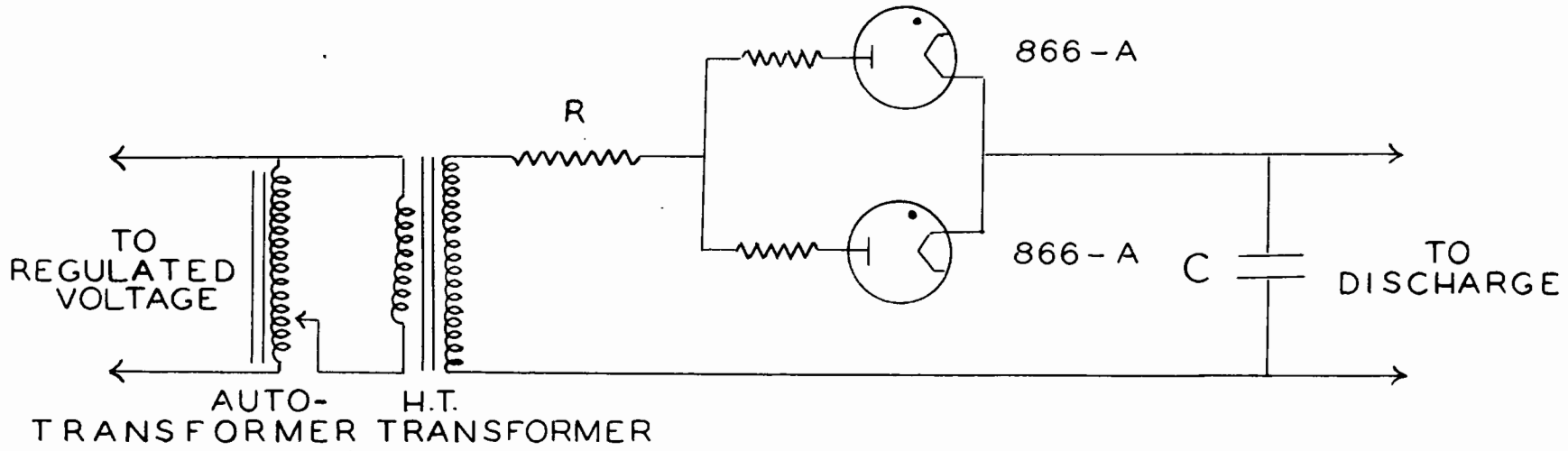
During experiments with ethylene, the trap H was simply immersed in liquid nitrogen. The products of interest in this study, hydrogen cyanide and cyanogen, were quantitatively removed from the gas stream. Similarly, excess reactant from the ammonia reaction was all retained in such a trap.

The discharge circuit is shown in Figure 3. A half-wave rectifier, using two 866-A tubes in parallel, charged the capacitor C until at the breakdown voltage of the gas in the discharge tube, the capacitor discharged very quickly and the cycle was repeated. The capacitance of C could be varied to control the energy input and a variable resistance R controlled the time constant of the circuit. The rate at which C became charged could also be controlled by the autotransformer in the primary of the plate transformer. Voltage regulated power and line isolation were provided by two Sola constant voltage transformers.

At the start of each experiment with the spherical reaction vessel, the discharge was turned on and the temperature at a thermocouple well in the active nitrogen stream allowed to reach a steady value. Equal temperatures were assumed to mean equal concentrations of active nitrogen. The discharge frequency throughout these experiments was held at 12 flashes per second as determined with an oscilloscope which recorded the voltage on a voltage divider across the capacitor C. The stepwise charging rate of the half-wave rectifier provided a convenient time base. Unfortunately the voltage divider appeared to reduce the long term stability of the discharge rate and was disconnected during most of the experiments. An improved method was used with the second long tube reaction vessel. A type 929 phototube was placed near the discharge tube, the pulse caused by each discharge being recorded by a Brush recording oscillograph. The discharge frequency was held at 20 flashes per second during these later experiments.

FIGURE 3

DIAGRAM OF DISCHARGE CIRCUIT


866 - A
R
866 - A
C
TO
REGULATED
VOLTAGE
TO
DISCHARGE
AUTO-
TRANSFORMER
H.T.
TRANSFORMER

ANALYSIS

The analytical procedure used by Willey and Rideal (24) assumed that all of the oxygen formed in the active nitrogen NO reaction combined with excess nitric oxide in the cold trap to produce NO_2. An attempt was made to apply their method in the present study; but after repeated checks of the method with known amounts of nitric oxide and oxygen, it was necessary to conclude that the method was incapable of reproducible results.

Considerable time was spent in efforts to develop a satisfactory modification of the method. In outline, the approach was to sample the effluent gases with a 1 liter bulb which had been evacuated before the experiment and to oxidize the nitrogen oxides to nitric acid via the cycle

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2$$

The nitric acid formed was then taken up in base and determined by back titration. After many refinements of the technique, it was finally possible to obtain between 85 and 100% of the theoretical yield of nitric acid, but better accuracy could not be achieved. Similar experiments with ammonia and careful checking of each step showed that

the difficulty was due to incomplete oxidation to nitric acid.

The method finally used consisted of the following. The products of the nitric oxide reaction, condensed in the cold trap during an experiment, were distilled into a bulb of known volume J to which was attached a manometer M_4. An excess of oxygen was admitted and the mixture alternately expanded and condensed to insure complete oxidation of any unreacted nitric oxide. The nitrogen dioxide was then frozen out, any excess oxygen pumped off, the nitrogen dioxide expanded and its pressure measured at 25°C. Pressure concentration relations for nitrogen dioxide were obtained from Verhoek and Daniels (98). Several experiments with a known quantity of pure nitric oxide showed that the method was capable of analytical data within $\pm 2\%$ of the absolute amount of NO taken.

The products of the nitrogen dioxide reaction were distilled into this same bulb J. A known pressure of oxygen p_1 was admitted, all nitric oxide in the mixture oxidized and the pressure p_2 measured. Unreacted oxygen was then pumped off while the other products were kept at liquid nitrogen temperature and the pressure p_3 determined. The partial pressure of nitric oxide could then be obtained from the expression

$$p_{NO} = 2\ (p_1 + p_3 - p_2)$$

Finally the gases were again condensed and the bulb surrounded with a dry ice-acetone bath. Nitrous oxide was pumped off and the pressure of

nitrogen dioxide p_4 measured. The partial pressure of nitrous oxide was given by p_3-p_4, while p_4 gave the sum of nitric oxide and unreacted nitrogen dioxide. All pressure measurements were made at 25°C.

To determine the hydrogen cyanide produced in the ethylene reaction, the products were distilled from the cold trap into a removable absorber containing 15 ml. of distilled water and frozen with liquid nitrogen. A layer of carbon tetrachloride frozen around the products trap during the distillation and rapid warming of the water in the absorber after the distillation, prevented polymerization of the hydrogen cyanide. The trap was then opened to the atmosphere and the hydrogen cyanide determined argentimetrically according to the Liebig-Deniges method (99). Cyanogen was determined according to the method of Wallis and Rhodes (100); details of the method may be found in a thesis by Klassen (74).

Unreacted ammonia was determined by distilling it into a removable absorber containing a known amount of 0.1 N acid and back titrating with base.

RESULTS

NITRIC OXIDE

When nitric oxide was introduced into the active nitrogen stream in very small quantities, a purple-blue glow became mixed with the yellow Lewis-Rayleigh afterglow immediately below the nitric oxide inlet. The blue afterglow was very long-lived and, in the absence of a cold trap in the line, could be seen to the pump. The "coexistence" of the yellow and blue afterglows could be very convincingly demonstrated by placing a coil of silver wire in the gas stream. The silver completely quenched the blue glow but left yellow afterglow to extend beyond it, apparently unaffected. On increasing the flow rate of nitric oxide, the blue glow became more intense while the yellow glow diminished until it could no longer be discerned beyond the silver wire. A further increase in the nitric oxide flow rate brought about an abrupt change. The region of blue glow contracted to but a few millimeters below the reactant inlet and was then replaced by a yellow-green afterglow. This green glow was equally as long-lived as the blue, and could also be quenched by a cold trap or a silver wire. Still larger flow rates of nitric oxide caused the blue layer to be reduced to a thin "disk" which never completely disappeared.

It was found that, at any flow rate of nitric oxide insufficient to cause the green afterglow, only ozone could be condensed

in the cold trap. The silver wire ahead of the trap prevented ozone formation but no measurable quantities of nitrogen oxides were recovered. At flow rates where the green afterglow was produced, nitric oxide and nitrogen dioxide were both recovered. No nitrous oxide was recovered at any flow rate of nitric oxide.

NITROGEN DIOXIDE

As with nitric oxide, low flow rates of nitrogen dioxide, admitted to the active nitrogen stream, caused a blue glow which became more intense with increasing nitrogen dioxide flow rate. An abrupt transition again took place to the yellow-green afterglow, with only a thin layer of the blue glow persisting between the yellow nitrogen afterglow and the green glow. Further increase in the reactant flow caused the green afterglow also to be reduced suddenly to a thin, barely visible layer beyond which point no glow was visible. The ratio of the nitrogen dioxide flow rate at which the green glow "cut off" to the nitrogen dioxide flow rate at which the green glow appeared, was determined at three different energy inputs to the discharge tube. This ratio was found to be 1.8 reproducible to within 0.1.

At flow rates of nitrogen dioxide where only the blue afterglow could be seen, nitrous oxide was the only condensible product; the silver wire was placed ahead of the products trap to prevent ozone formation. In the region of the green afterglow and beyond, nitric oxide and nitrogen dioxide were recovered as well as nitrous oxide.

EFFECT OF POWER INPUT

The flow rate of molecular nitrogen, in these experiments with the spherical reaction vessel, was 180 micro-moles per second. With the discharge rate maintained at 12 flashes per second, the pressure in the reaction vessel was 1.67 mm. Variations in this pressure did not exceed 0.05 mm. when reactant was admitted.

The amount of nitric oxide destroyed was determined for each of five different energy inputs to the discharge tube. The energy input was varied over a range of 16 to 1 by changing the capacitance in the discharge circuit; 0.25, 0.50, 1.0, 2.0 and 4.0 microfarads were the actual values used. The results are shown in Table I and Figure 4. It must be pointed out that any nitrogen dioxide recovered was considered equivalent to the same amount of nitric oxide recovered.

The maximal amounts of hydrogen cyanide produced in the active nitrogen-ethylene reaction were determined under the same conditions as those used for measuring the destruction of nitric oxide. All determinations were made in the range of 300° to 400°C where hydrogen cyanide yields were independent of temperature. The results are shown in Table II and Figure 5. The rate of cyanogen production was measured in a series of experiments with 2 microfarads in the discharge circuit with the results shown in Table III. The rate of cyanogen production, under conditions of limiting hydrogen cyanide production, was 0.1 micro-moles per second and thus equivalent to 0.2

TABLE I

REACTION OF ACTIVE NITROGEN WITH NITRIC OXIDE

Capacitance μfd	Temp. °C	NO Flow Rate (mole/sec.)	NO destroyed (mole/sec.)
0.25	400	10.9×10^{-6}	2.7×10^{-6}
	400	11.0	2.9
	400	15.9	3.4
	400	19.9	3.5
	400	23.9	3.3
0.50	400	21.4	6.8
	400	25.4	7.0
	400	30.0	7.4
	400	34.2	7.8
1.0	400	21.0	11.0
	400	30.0	11.8
	400	34.8	12.0
2.0	300	21.0	15.6
	300	30.0	16.0
		31.0	16.0
	400	34.5	16.0
4.0	400	24.4	21.1
	400	28.6	21.9
	400	33.0	21.3
	400	33.5	21.6

FIGURE 4

NO Flow Rate vs NO destroyed

□ 0.25 μfd.

▼ 0.50 μfd.

▽ 1.0 μfd.

● 2.0 μfd.

○ 4.0 μfd.

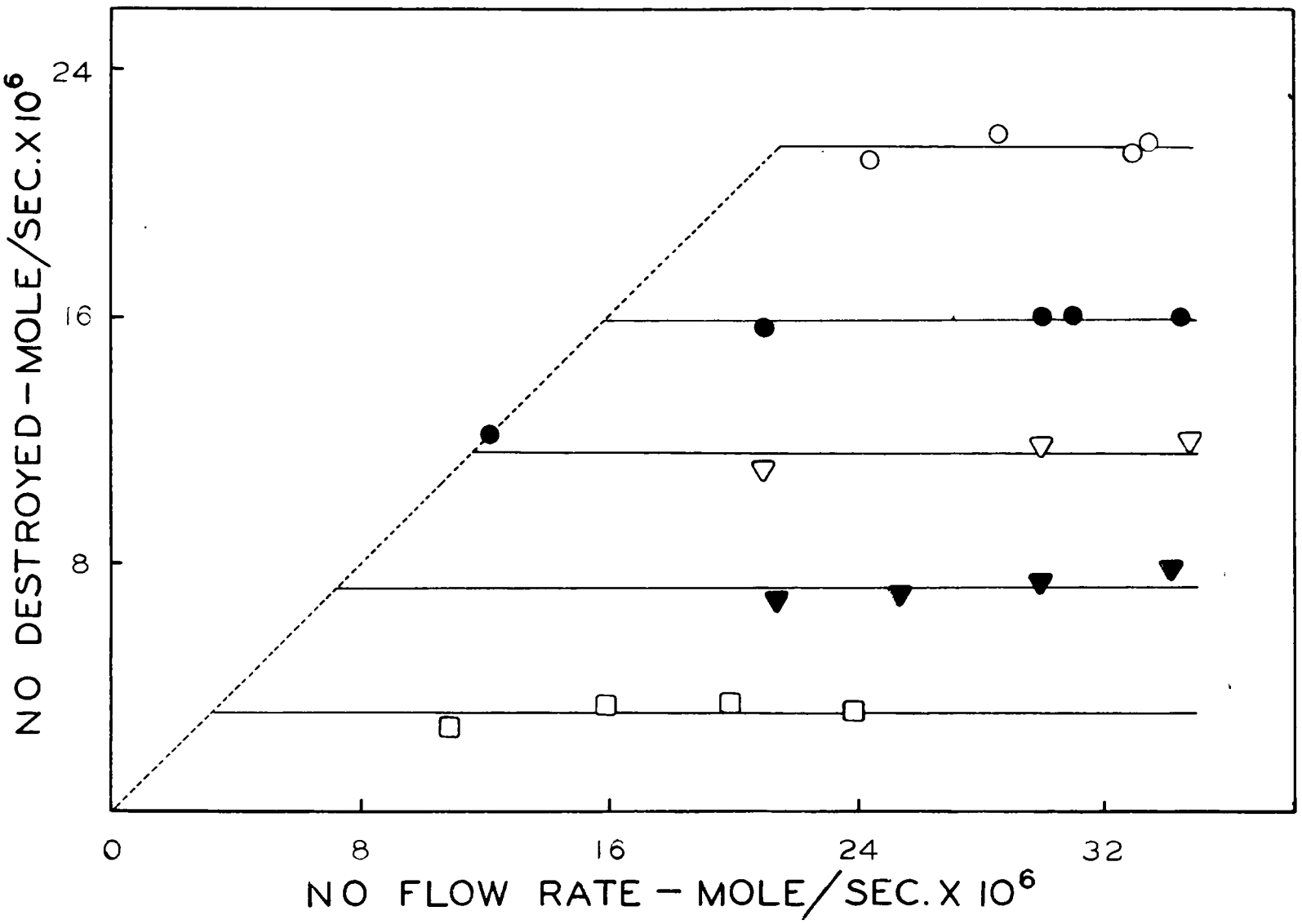

NO DESTROYED – MOLE/SEC. X 10⁶
24
16
8
0
8
16
24
32
NO FLOW RATE – MOLE/SEC. X 10⁶

TABLE II

REACTION OF ACTIVE NITROGEN WITH ETHYLENE

Capacitance μfd	Temp. °C	C_2H_4 Flow Rate (mole/sec.)	HCN produced (mole/sec.)
0.25	400	4.8×10^{-6}	2.2×10^{-6}
	400	9.8	2.1
	400	10.1	1.8
	400	24.1	2.3
0.50	400	13.7	4.1
	400	15.4	4.3
	400	24.3	4.2
1.0	400	10.1	7.8
	400	17.1	7.8
	400	24.2	7.9
2.0	400	2.0	3.0
	300	3.6	5.9
	300	6.6	9.1
	300	6.9	10.1
	300	10.3	10.7
	300	10.3	10.6
	300	13.7	10.9
	300	17.1	11.2
	300	20.6	11.3
	440	24.2	11.5
	440	27.8	11.1
	440	33.4	11.2
4.0	400	6.6	9.5
	400	10.0	11.9
	400	13.3	12.8
	400	13.7	12.8
	400	16.9	13.3
	400	17.1	14.7
	400	17.1	14.8
	400	20.2	13.9
	400	23.6	14.5
	400	33.0	14.1

TABLE III

REACTION OF ACTIVE NITROGEN WITH ETHYLENE

Capacitance μfd	Temp. °C	C_2H_4 Flow Rate (mole/sec.)	C_2N_2 produced (mole/sec.)
2.0	400	1.9×10^{-6}	0.15×10^{-6}
	400	3.6	0.225
	400	4.9	0.225
	400	6.6	0.17
	400	8.3	0.17
	400	10.2	0.11
	400	13.8	0.10
	400	28.0	0.08

FIGURE 5

C_2H_4 Flow Rate vs HCN produced

□ 0.25 μfd.

▼ 0.50 μfd.

▽ 1.0 μfd.

● 2.0 μfd.

○ 4.0 μfd.

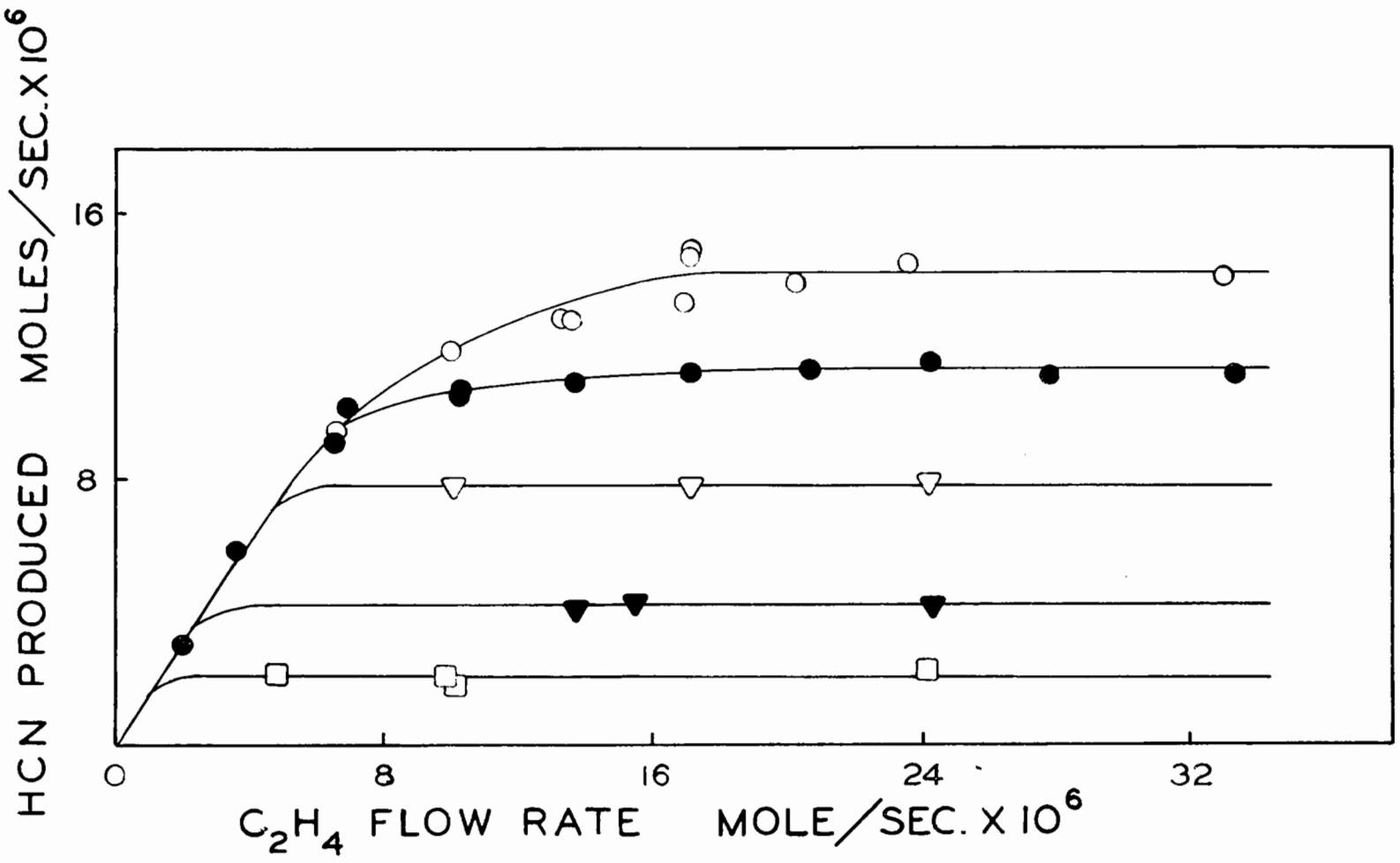

HCN PRODUCED MOLES/SEC. X 10^6
16
8
0
8
16
24
32
C2H4 FLOW RATE MOLE/SEC. X 10^6

FIGURE 6

NO destroyed and HCN produced vs

Power Input

○ NO

□ HCN

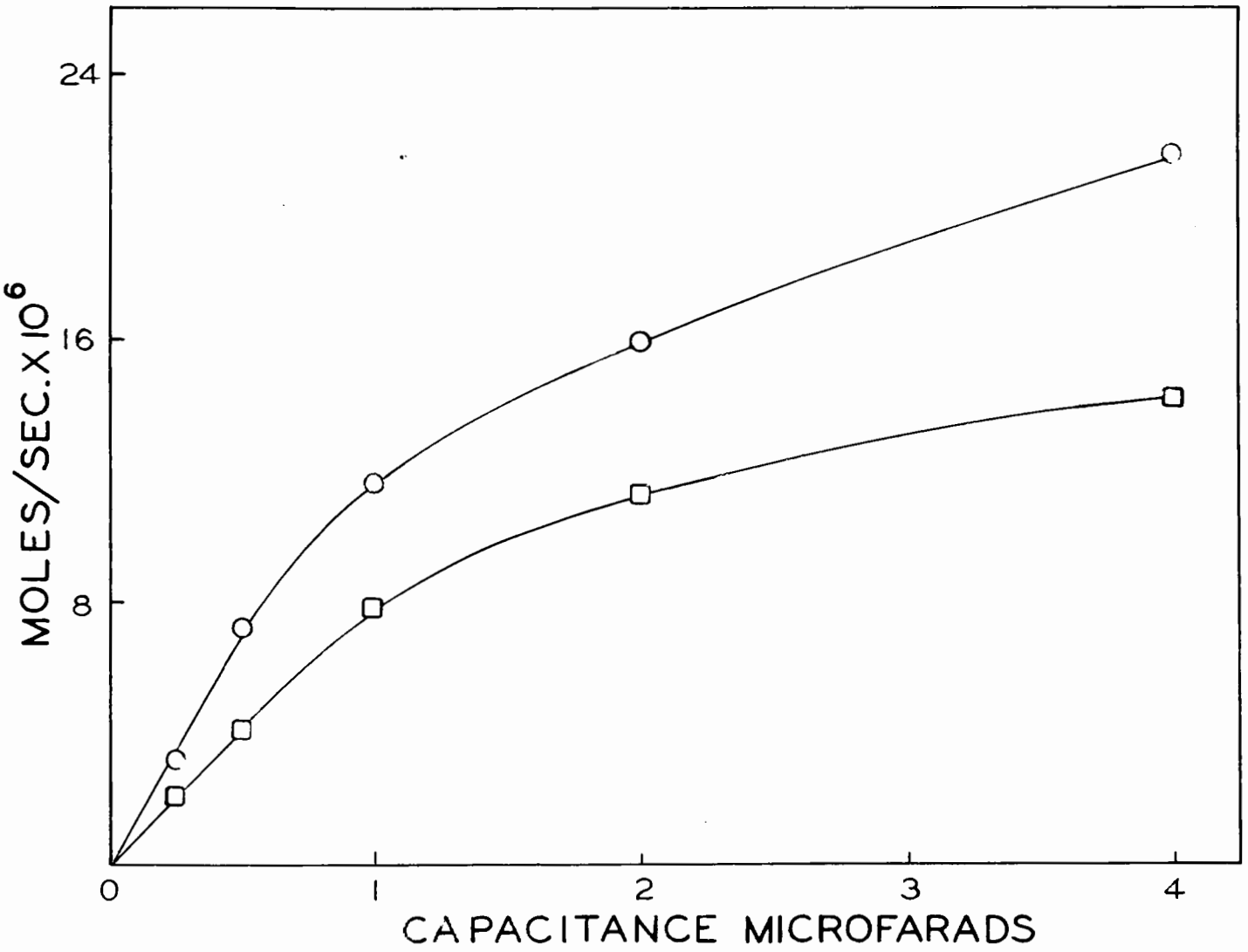

24
16
8
MOLES/SEC. X 10^6
0
1
2
3
4
CAPACITANCE MICROFARADS

TABLE IV

Capacitance μfd	NO destroyed (mole/sec.)	HCN produced (mole/sec.)	Ratio $\frac{NO}{HCN}$
0.25	3.2×10^{-6}	2.1×10^{-6}	1.52
0.50	7.2	4.2	1.71
1.0	11.6	7.8	1.49
2.0	15.9	11.3	1.41
4.0	21.5	14.2	1.51

micro-moles per second of hydrogen cyanide. Since this was within the experimental error of the hydrogen cyanide determination, the contribution of cyanogen was neglected.

A comparison of the amount of nitric oxide destroyed and the amount of hydrogen cyanide produced as a function of the capacitance in the discharge circuit is shown in Figure 6. As may be seen in Table IV, the ratio of nitric oxide destroyed to hydrogen cyanide produced was, within the limits of experimental error, constant over a wide range of active nitrogen flow rates.

COMPARISON OF THE NO, NO_2, NH_3 AND C_2H_4 REACTIONS.

With a molecular nitrogen flowrate of 170 micro-moles per second and a discharge rate of 20 flashes per second, the pressure in the second long tube reaction vessel was 1.90 mm. Small variations, of the order of 0.05 mm., at different reactant inlets, were attributed to turbulence caused by the inlets themselves.

In Table V and Figure 7 are shown the amounts of nitric oxide destroyed at each inlet of the reaction tube. Where no temperature is indicated, the walls of the reaction tube were not heated and the temperature not measured. From other studies in this laboratory with a similar reaction tube,* it has been found that, in the absence of reactant, the temperature of the gas stream ranges from approximately

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* Private communication from Dr. R. Back

100°C at the top to some 40° C at the bottom inlet. No change in the amount of nitric oxide destroyed was observed over the range from 100° to 370°C at the first inlet.

The amounts of ammonia destroyed at different distances downstream are shown in Table VI and Figure 8. The reaction tube was not heated during these experiments.

Table VII and Figure 9 show the maximal hydrogen cyanide production at the different inlets of the reaction tube. All these experiments were made with the walls immediately below the reactant inlet heated to 300°C or higher.

The results of experiments with nitrogen dioxide at the first reactant inlet, with an unheated reaction tube and with the tube heated to 300°C, are shown in Table VIII and Figures 10, 11 and 12.

Figure 13 shows the amounts of nitric oxide and ammonia destroyed, and of hydrogen cyanide produced as functions of distance below the first reactant inlet. The ratio of nitric oxide destroyed to hydrogen cyanide produced, given in Table IX, appeared to increase with distance from the discharge tube. However the change was slight and of the same order of magnitude as the experimental uncertainty.

The ratio of nitric oxide destroyed to hydrogen cyanide formed was also studied briefly as a function of pressure, at the first inlet only. At a pressure of 0.9 mm., one half the normal operating

TABLE V

REACTION OF ACTIVE NITROGEN WITH NITRIC OXIDE

Distance below 1st Inlet - cm.	Temp. °C	NO Flow Rate (mole/sec.)	NO destroyed Mole/sec.)
0		23.8×10^{-6}	19.3×10^{-6}
	300	23.8	18.0
	300	28.1	18.6
		28.3	18.1
		28.4	18.3
		29.0	18.7
	300	32.7	18.6
	300	32.8	18.7
	370	33.4	18.9
	300	37.8	19.0
20		19.8	14.9
		24.2	14.2
		29.2	14.8
40		15.1	11.3
		19.9	11.5
		23.8	10.9
60		15.6	9.9
		19.5	9.4
		24.0	9.4
80		15.6	8.6
		19.5	8.9
120		15.1	6.7
		19.7	7.1

FIGURE 7

NO Flow Rate vs NO destroyed

○	0	cm. below 1st inlet
△	0	cm. (300°C)
●	20	cm.
▲	40	cm.
▽	60	cm.
▼	80	cm.
□	120	cm.

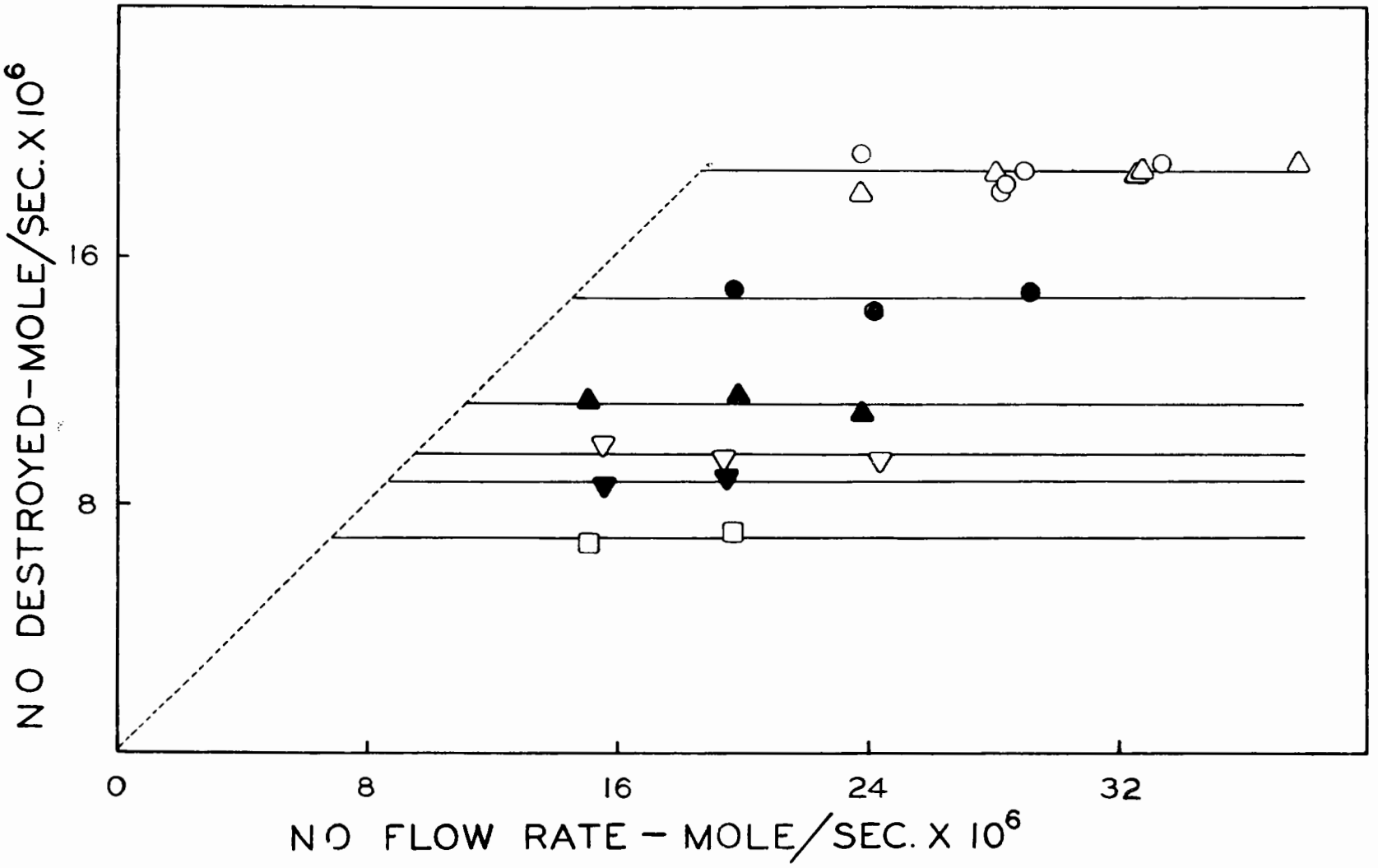

NO DESTROYED-MOLE/SEC. X 10^6
16
8
0
8
16
24
32
NO FLOW RATE - MOLE/SEC. X 10^6

TABLE VI

REACTION OF ACTIVE NITROGEN WITH AMMONIA

Distance below 1st Inlet - cm.	NH_3 Flow Rate (mole/sec.)	NH_3 destroyed (mole/sec.)
0	10.2×10^{-6}	2.4×10^{-6}
	16.8	2.3
20	10.0	1.7
	16.6	1.4
60	10.3	0.9
	16.2	0.9
120	6.9	0.4
	10.0	0.4
	15.0	0.6

TABLE VII

REACTION OF ACTIVE NITROGEN WITH ETHYLENE

Distance below 1st Inlet - cm.	Temp. °C	C_2H_4 Flow Rate (mole/sec.)	HCN produced (mole/sec.)
0	300	12.2×10^{-6}	13.5×10^{-6}
	300	13.5	13.9
	300	15.7	14.1
	300	19.4	13.9
20	310	11.9	10.5
	360	15.3	10.4
40	350	9.8	8.2
	390	13.8	8.3
60	340	8.4	7.0
	325	11.8	7.0
80	300	8.1	6.1
	320	11.8	6.3
120	380	8.5	4.7
	300	11.8	4.5

FIGURE 8

NH_3 Flow Rate vs NH_3 destroyed

○ 0 cm. below 1st inlet

● 20 cm.

▲ 40 cm.

□ 120 cm.

FIGURE 9

C_2H_4 Flow Rate vs HCN produced

○ 0 cm. below 1st inlet

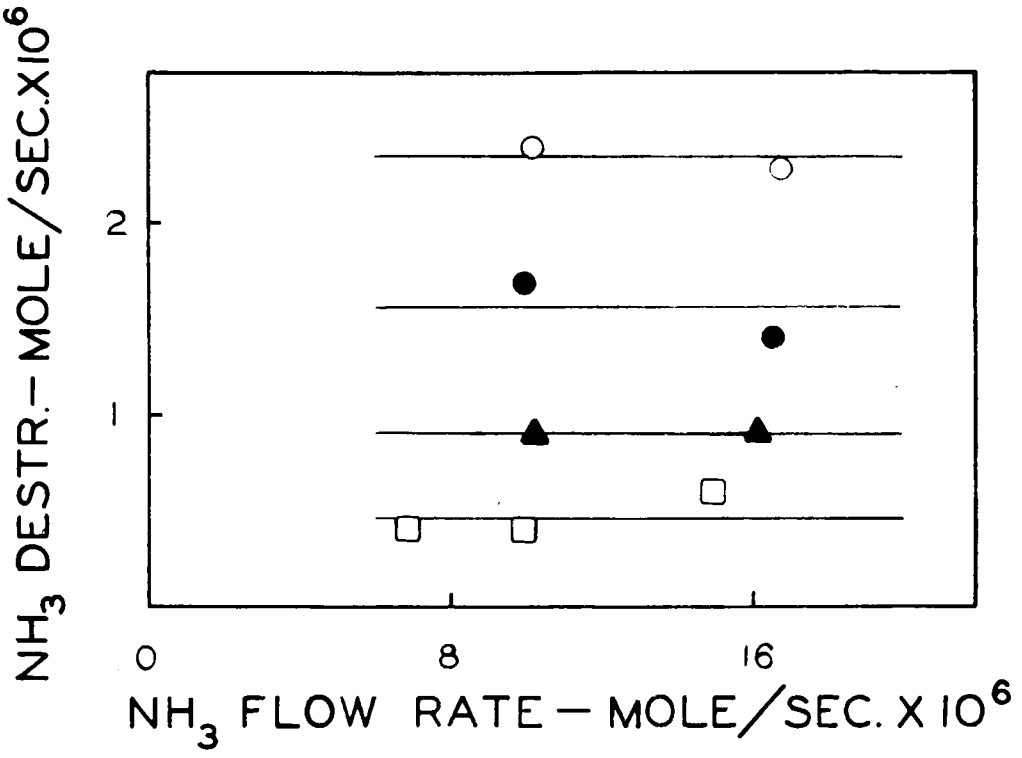
● 20 cm.

▲ 40 cm.

▽ 60 cm.

▼ 80 cm.

□ 120 cm.


NH3 DESTR.– MOLE/SEC.X10^6
2
1
0
8
16
NH3 FLOW RATE – MOLE/SEC. X 10^6

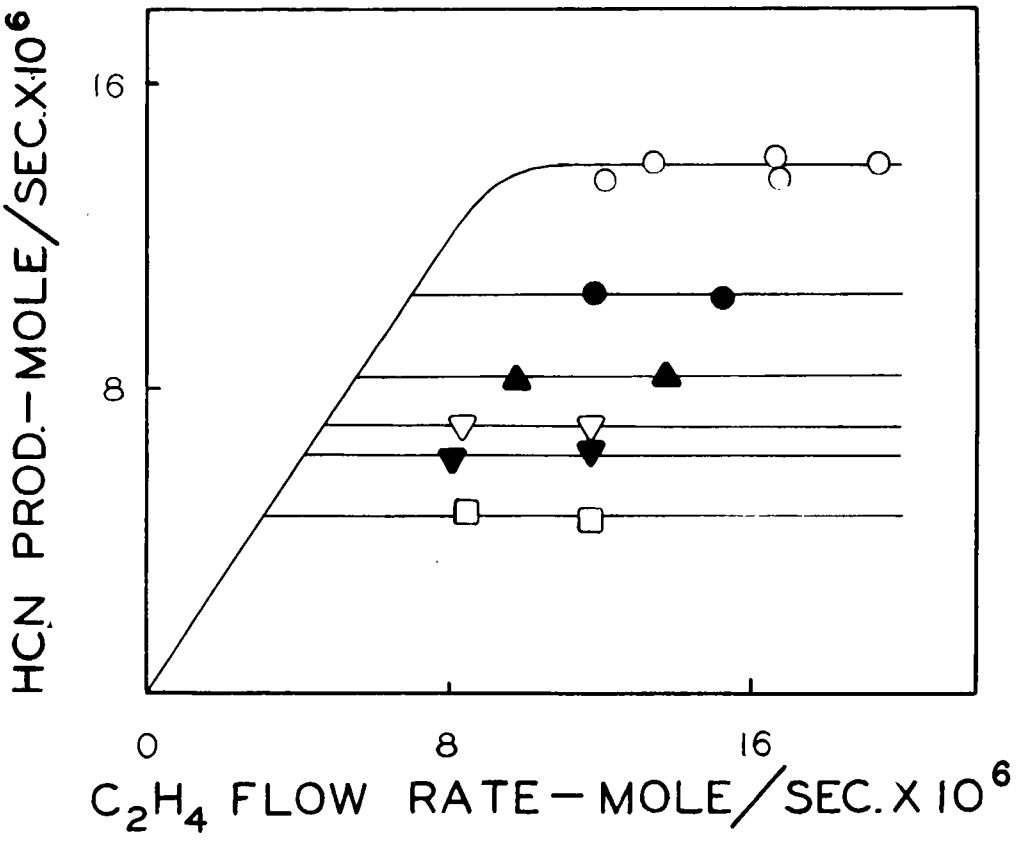

HCN PROD.– MOLE/SEC.X10^6
16
8
0
8
16
C2H4 FLOW RATE – MOLE/SEC. X 10^6

TABLE VIII

REACTION OF ACTIVE NITROGEN WITH NITROGEN DIOXIDE.

Temp. °C	NO_2 Flow Rate mole/sec.	NO recovered mole/sec.	NO_2 recovered mole/sec.	NO + NO_2 recovered mole/sec.	N_2O produced mole/sec.	N-oxides loss mole/sec.	N_2O + Loss N-oxides mole/sec.	O_2 produced mole/sec.
300	7.6×10^{-6}	- -	- -	0.1×10^{-6}	2.5×10^{-6}	5.0×10^{-6}	7.5×10^{-6}	6.3×10^{-6}
300	12.5	- -	- -	0.2	3.3	9.3	12.3	11.3
300	17.6	1.9	2.3	4.1	3.6	9.9	13.5	12.5
	17.6	2.0	1.1	3.1	4.8	9.7	14.5	13.1
300	23.0	3.9	4.7	8.6	4.3	10.1	14.4	14.2
300	23.0	4.7	4.8	9.5	4.3	9.2	13.5	13.7
300	28.8	6.3	8.7	15.0	4.5	9.3	13.8	14.7
	28.8	8.2	6.5	14.7	4.8	9.3	14.1	15.8
	34.2	8.2	11.6	19.8	4.4	10.0	14.4	16.3
	34.2	9.9	10.3	20.2	4.6	9.4	14.0	16.6
	39.9	10.8	15.6	26.4	4.9	8.6	13.5	16.5
	45.5	11.7	19.0	30.7	5.2	9.1	14.3	18.1
	45.5	11.9	19.9	31.8	4.9	8.8	13.7	17.2
300	45.5	12.6	19.5	32.1	5.2	8.2	13.4	17.1
	51.0	13.0	23.2	36.2	5.2	9.6	14.8	18.7

FIGURE 10

NO_2 Flow Rate vs

△ NO_2 recovered

● NO_2 recovered (300°C)

○ NO + NO_2 rec'd

▽ NO + NO_2 rec'd (300°C)

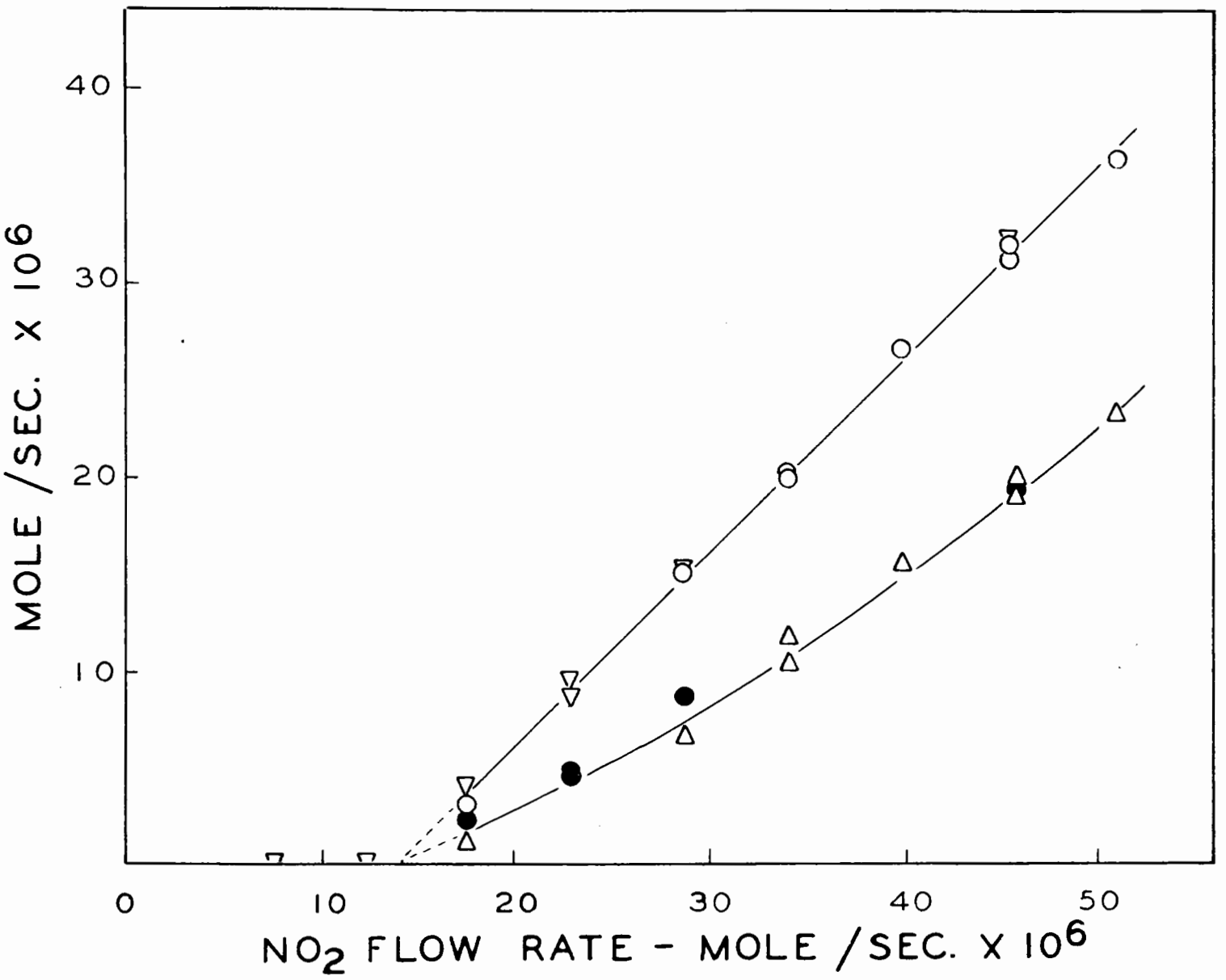

40
30
20
10
MOLE /SEC. X 106
0
10
20
30
40
50
NO2 FLOW RATE - MOLE /SEC. X 10^6

FIGURE 11

NO_2 Flow Rate vs

○ N_2O produced

▽ N_2O produced (300°C)

● N_2O + N oxides lost

△ N_2O + N oxides lost (300°C)

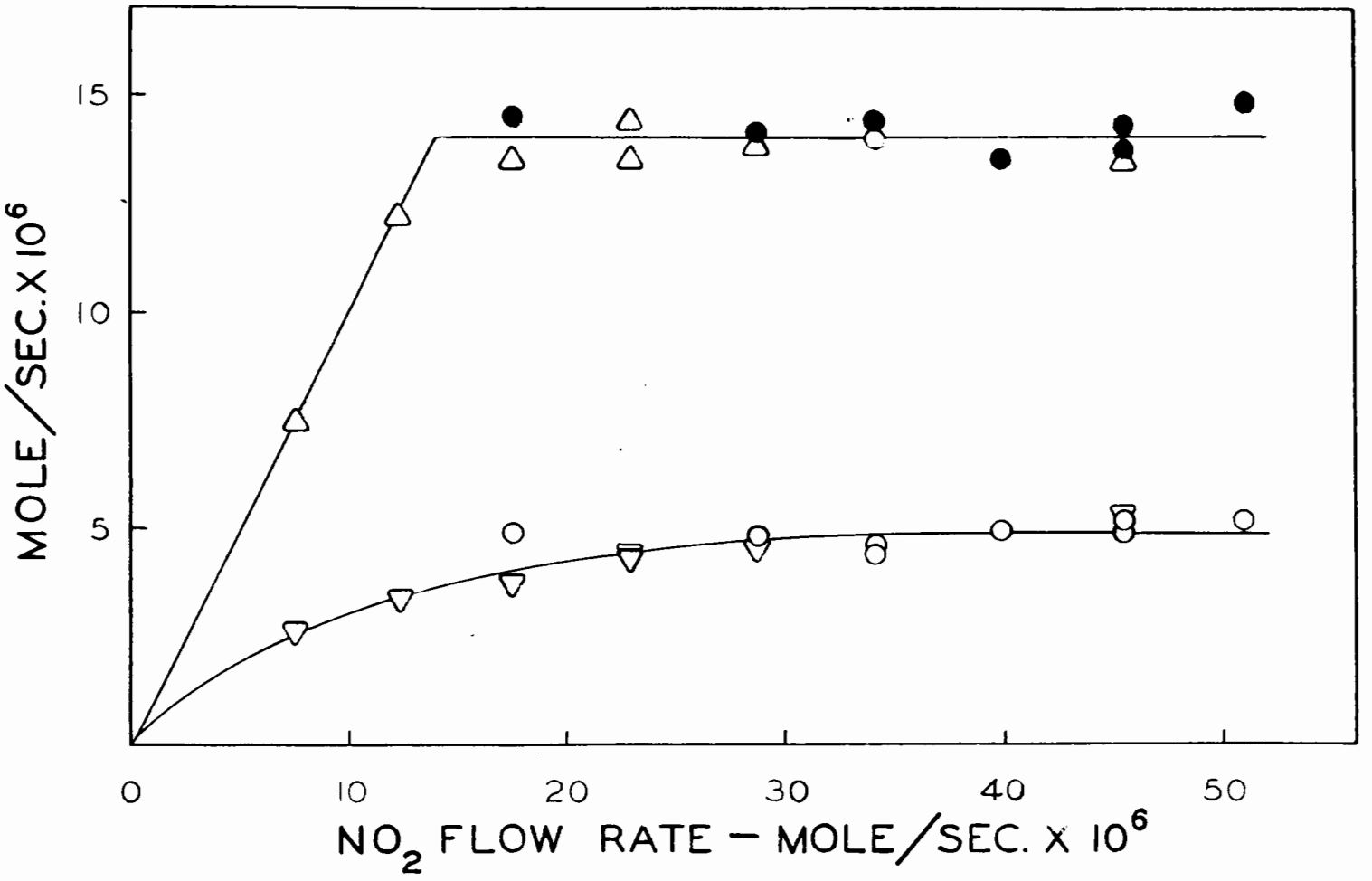

15
10
5
MOLE/SEC. X 10^6
0
10
20
30
40
50
NO2 FLOW RATE – MOLE/SEC. X 10^6

FIGURE 12

NO_2 Flow Rate vs

● NO recovered

▽ NO recovered (300°C)

○ O_2 produced

△ O_2 produced (300°C)

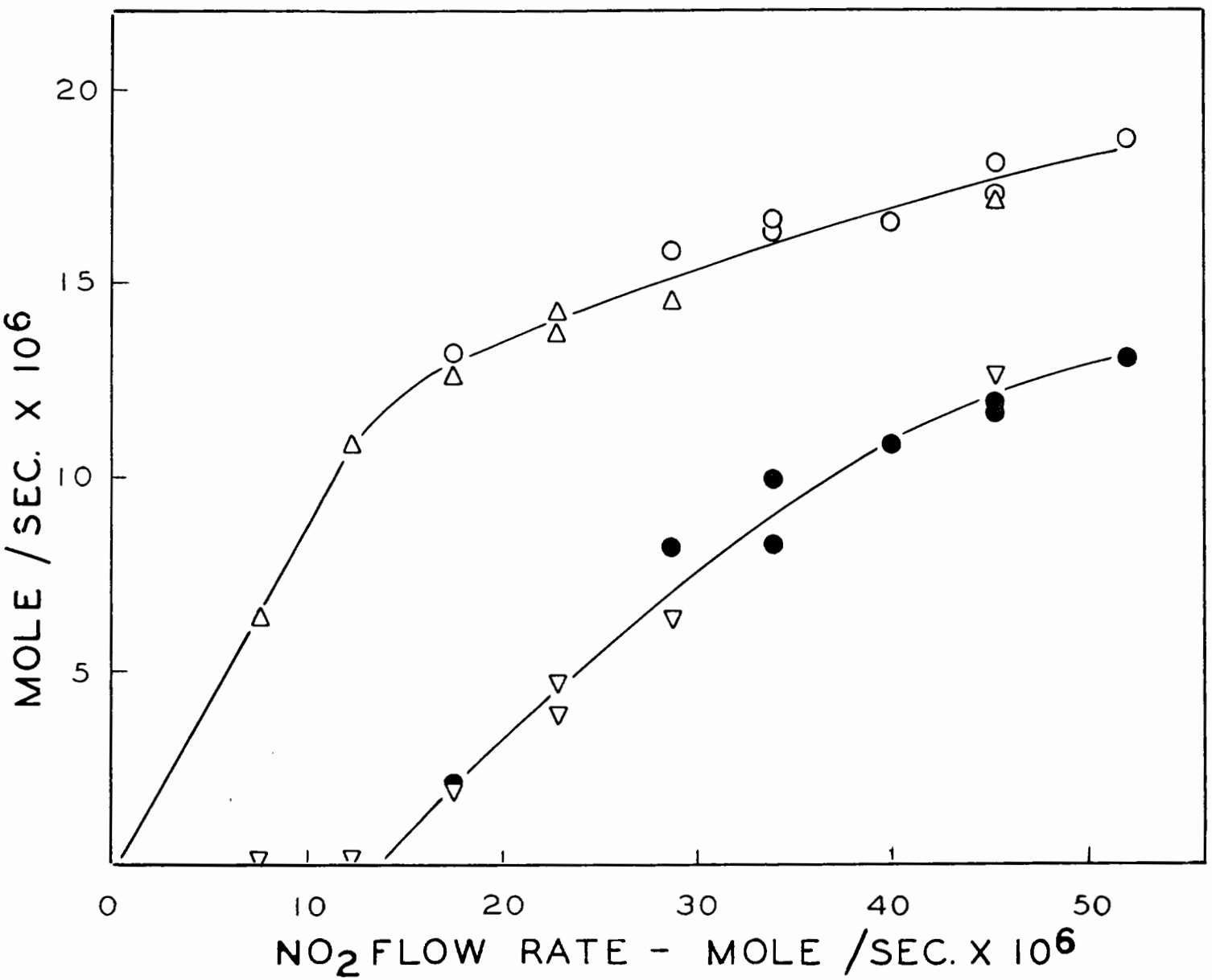

20
15
10
5
MOLE /SEC. X 10⁶
0
10
20
30
40
50
NO2 FLOW RATE - MOLE /SEC. X 10⁶

FIGURE 13

Distance below 1st Inlet vs

○ NO destroyed

□ HCN produced

▽ NH_3 destroyed

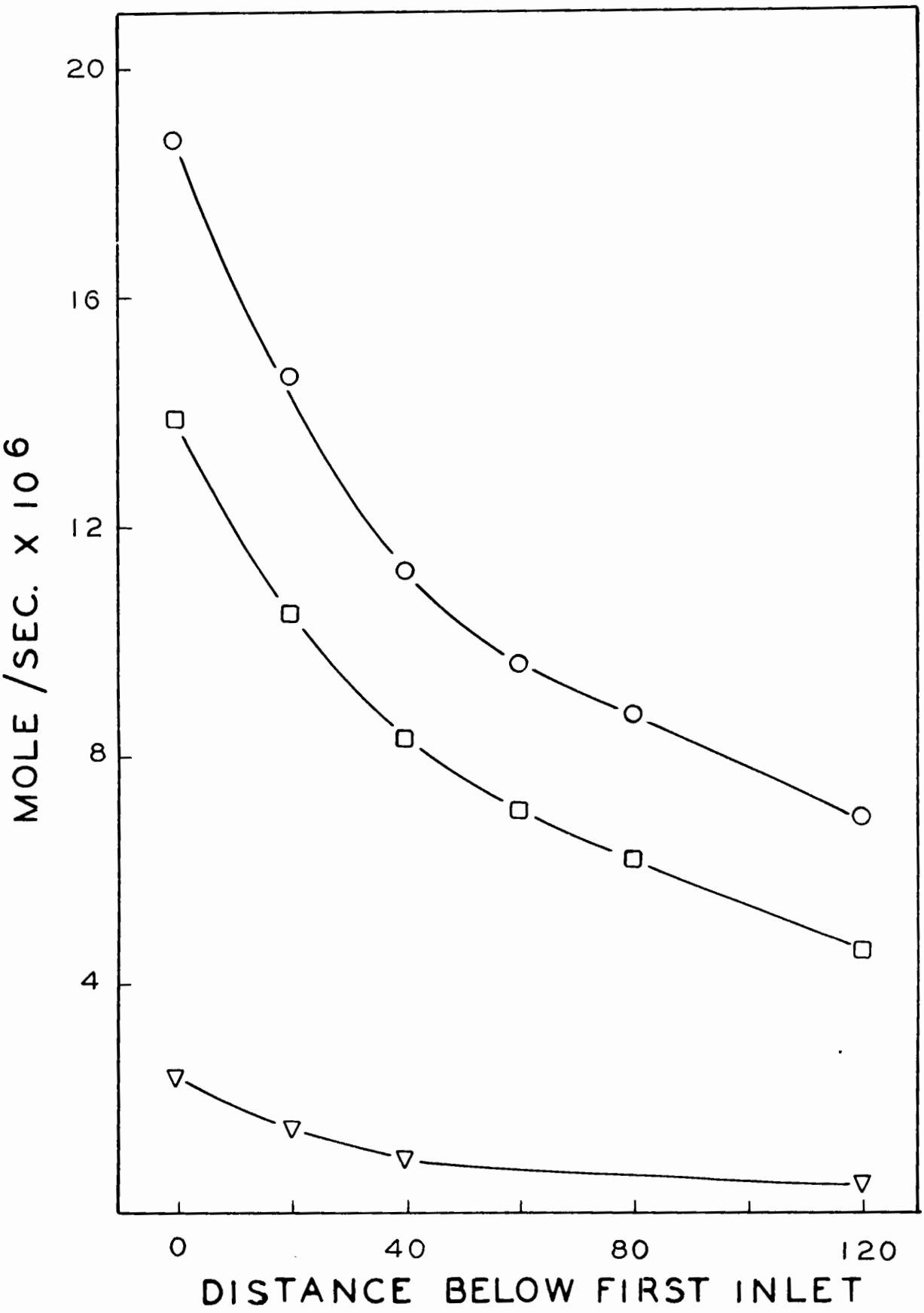

20
16
12
8
4
MOLE /SEC. X 10 6
0
40
80
120
DISTANCE BELOW FIRST INLET

TABLE IX

Distance below 1st. Inlet - cm.	NO destroyed (mole/sec.)	HCN produced (mole/sec.)	Ratio $\frac{NO}{HCN}$
0	18.7×10^{-6}	13.9×10^{-6}	1.35
20	14.6	10.5	1.39
40	11.2	8.3	1.36
60	9.6	7.0	1.37
80	8.7	6.2	1.40
120	6.9	4.6	1.50

pressure, the admission of reactant sensibly altered the total pressure and the ratio of 1.4 which was measured is probably of doubtful significance. The ratio was also determined at a total pressure of 3.8 mm. which was almost twice normal, and a value of 1.73 found. Experiments at still higher pressures were unfortunately not possible owing to the difficulties of obtaining a stable discharge in this region.

The characteristic emission spectra observed when these two oxides of nitrogen were present in concentrations less than and greater than that of the active nitrogen, suggested a possible method of determining rate constants for the reactions.

The β bands of NO in these systems are known (90) to be due to the reaction

$$N + O \longrightarrow NO^{*} \longrightarrow NO + h\nu$$

Their appearance in any portion of the apparatus is therefore an indication that nitrogen atoms are present in that portion. This blue glow was visible below the reactant inlet at all flowrates of NO or NO_2. However the yellow-green glow due to

$$NO_2^{*} \longrightarrow NO_2 + h\nu$$

was visible only when inflowing NO or NO_2 were in excess of the active nitrogen, i.e. when unreacted oxides were present. This simultaneous appearance of the green glow with the recovery of reactant was confirmed many times and might serve as a "titration" for active nitrogen analogous to the titration of oxygen atoms with NO_2 proposed by

Kaufman (94). It would appear therefore that the process leading to emission from NO_2^* is slower than the reactions of nitrogen atoms with either NO or NO_2 and does not occur in the presence of atomic nitrogen. This in turn means that essentially all the active nitrogen reaction occurs in the region where the β bands of NO are visible. A measure of the reaction time is therefore possible from the length of this region and the linear velocity of the gas in the reaction tube.

If we assume a bimolecular reaction mechanism and integrate the rate expression on the assumption of complete lateral mixing and negligible axial mixing, we obtain the expression

$$k = \frac{1}{t(N_i - R_i)} \ln \frac{R_i \cdot N_f}{N_i \cdot R_f}$$

where: k = second order rate constant

t = reaction time

N_i, R_i = initial concentration of active nitrogen and reactants

N_f, R_f = concentration of active nitrogen and reactants after time t

The demarcation between the region of blue glow and those of yellow nitrogen afterglow and green NO_2^* glow, proved to be quite sharp. The length of the blue region along the axis of the reaction tube could easily be measured in a darkened room. It was found to be a few millimeters long. The results are listed in detail in Table X together with

TABLE X

SECOND ORDER RATE CONSTANTS

Nitric Oxide Reaction

Active Nitrogen Flow Rate (moles/sec.)	Nitric Oxide Flow Rate (moles/sec.)	Length of Blue Zone mm.	Reaction Time sec.	Rate Constant Second order (cc./mole sec.)
18.7×10^{-6}	20×10^{-6}	4	2.5×10^{-4}	4.0×10^{12}
18.7×10^{-6}	40×10^{-6}	3	1.9×10^{-4}	1.2×10^{12}

Collision Number 2.0×10^{14} cc./mole sec.

Nitrogen Dioxide Reaction

Active Nitrogen Flow Rate (moles/sec.)	Nitrogen Dioxide Flow R (moles/sec.)	Length of Blue Zone mm.	Reaction Time sec.	Rate Constant Second order (cc./mole sec.)
14.0×10^{-6}	18×10^{-6}	2	1.2×10^{-4}	5.3×10^{12}
14.0×10^{-6}	28×10^{-6}	1.5	1.0×10^{-4}	4.5×10^{12}

Collision Number 2.6×10^{14} cc./mole sec.

Total flowrate = 200×10^{-6} moles/sec.

Total pressure = 2.2 mm.

Temperature = 500°K

Linear velocity = 16 meters/sec.

values for any other data used in the calculation of rate constants.

A temperature of 500°K was assumed on the basis of thermocouple measurements obtained at similar flow rates of reactants in the spherical reaction vessel. The linear velocity of the gases was calculated from the cross section of the reaction tube and the volume flow but no correction was attempted for a possible velocity gradient between the center of the tube and the walls. The assumption of complete radial mixing was probably not entirely valid since the time of diffusion of a reactant molecule from the inlet to the wall was of the same order of magnitude as the reaction time. Since it was also assumed, in the calculation, that reaction was only 90% complete in the time measured, the values obtained for the rate constants should be regarded only as lower limits. Collision numbers were calculated from kinetic theory in the usual way, assuming collision diameters of 2.98 Å for nitrogen atoms (75), 3.4 Å for nitric oxide (101) and 5 Å for nitrogen dioxide.

DISCUSSION

Certainly the most striking fact revealed by the present study was that nitric oxide was destroyed by reaction with active nitrogen in significantly larger amounts than hydrogen cyanide was formed from the reaction with ethylene for conditions of maximal hydrogen cyanide production.

The reaction, at high temperature, of active nitrogen with excess ethylene has been considered, up to the present time, to "clean up" nitrogen atoms and, in the absence of significant quantities of any other nitrogenous products, the hydrogen cyanide formed, together with a small amount of cyanogen, have been taken as a measure of the concentration of nitrogen atoms.

A good deal of evidence supports this view. The ethylene reaction itself has the characteristics of a fast reaction, i.e. a plot of hydrogen cyanide formed versus flow rate of ethylene, shows that when active nitrogen is in excess, nearly all the carbon of the ethylene molecule is converted to hydrogen cyanide while, when ethylene is in excess, a maximal or plateau value of hydrogen cyanide formation is reached, which is thereafter independent of the ethylene flow rate. Moreover, a comparison of the maximal amount of hydrogen cyanide formed from ethylene with that formed from such diverse reactants as

propane (69), isobutane (71), cyclopentane (74), methyl and dimethyl acetylene (102) and methyl chloride (103) shows it to be the same, within the limits of experimental error, when all these reactions occur under conditions such that hydrogen cyanide formation is independent of temperature as well as reactant flow rate.

The lower concentration of active nitrogen indicated by the yield of hydrogen cyanide from ethylene, as compared with that inferred from the decomposition of nitric oxide, might be ascribed to loss of nitrogen atoms by recombination catalyzed by ethylene, for which evidence exists (81). The steps leading to loss of activity in active nitrogen through such recombination are probably

$$N + C_2H_4 \longrightarrow (NC_2H_4) \qquad (1)$$

$$N + (NC_2H_4) \longrightarrow N_2 + C_2H_4 \qquad (2)$$

The existence of an appreciable steady state concentration of reactant-nitrogen atom complex would effectively remove the three body restriction on the recombination of atoms. A mechanism of this type will evidently depend on the lifetime of the complex, a quantity which should in turn decrease with increasing temperature. This seemed to be confirmed by an increase in plateau values of hydrogen cyanide production to maximal values with increase of temperature. However the plateau value for hydrogen cyanide production from ethylene was temperature independent in the temperature range from 250° to 450°C which strongly suggests that in this temperature range no significant catalytic recombination occurs.

Loss of activity could also result, of course, if products of the reaction, rather than the reactant itself, catalyzed the recombination of nitrogen atoms. Methyl radicals resulting from the active nitrogen-ethylene reaction

$$N + C_2H_4 \longrightarrow HCN + CH_3 \qquad (3)$$

will probably not be important in this respect; the nitrogen atom-radical complex is very unlikely to have an appreciable lifetime since unlike reaction (3), the reaction

$$N + CH_3 \longrightarrow HCN + 2\,H \qquad (4)$$

is spin allowed. The presence of hydrogen atoms from reaction (4) might lead to consumption of active nitrogen without hydrogen cyanide production if NH radicals, and ultimately perhaps ammonia, were formed but remained undetected owing to destruction by active nitrogen. However, in a study of the reaction of active nitrogen with methane (68), the addition of atomic hydrogen was actually found to increase the rate of hydrogen cyanide production, presumably by increasing the concentration of methyl radicals by the reaction

$$H + CH_4 \longrightarrow CH_3 + H \qquad (5)$$

Moreover, the fast reaction of hydrogen atoms with ethylene to yield ethyl radicals should be strongly favoured with excess ethylene, and effectively remove hydrogen atoms from the system. Ethyl radicals should also react rapidly with active nitrogen to produce hydrogen cyanide.

Hydrogen cyanide, as a product of the active nitrogen-ethylene reaction, might catalyze recombination of nitrogen atoms, causing loss of

active nitrogen by the process

$$N + HCN \longrightarrow HCN_2 \qquad (6)$$

$$N + HCN_2 \longrightarrow N_2 + HCN \qquad (7)$$

However, such hydrogen cyanide catalyzed recombination of nitrogen atoms should become less important at very large flow rates of ethylene, whereas the optimal formation of hydrogen cyanide was unequivocally shown to be independent of ethylene flow rate. Hence, under such optimal conditions, only a negligible amount of product catalysis seems admissible. This has been substantiated in experiments where hydrogen cyanide was introduced into active nitrogen together with a hydrocarbon (104).

On the whole, therefore, it seems reasonable to assume that the optimal production of hydrogen cyanide from ethylene does correspond to the concentration of a species in active nitrogen that is capable of reaction with ethylene.

THE NITRIC OXIDE REACTION

The principal process in the reaction of active nitrogen with nitric oxide is undoubtedly

$$N + NO \longrightarrow N_2 + O + 75 \text{ kcal.}^{*} \qquad (8)$$

Emission of a blue colour, corresponding to the β bands of NO, known (89, 90) to be due to the reactions

$$N + O + M \longrightarrow NO(B^2\pi) + M \qquad (9)$$

$$NO(B^2\pi) \longrightarrow NO(X^2\pi) + h\nu \qquad (10)$$

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* Values for the heats of formation, together with their sources, used to calculate the heat of reaction for this and subsequent reactions may be found in the appendix

could be seen when NO was admitted to active nitrogen. The presence of oxygen atoms in the products has been observed mass spectrometrically (91). In the present study, their presence was indicated by a green emission in the presence of excess NO which undoubtedly resulted from the reaction of NO with atomic oxygen, and by formation of ozone in the cold trap in the absence of unreacted NO.

An alternative to reaction (8) is

$$N(^4S) + NO(^2\pi) \longrightarrow N_2O(^1\Sigma) + 114.5 \text{ kcal.} \quad (11)$$

However this reaction is spin forbidden and must indeed be very much slower than the spin allowed reaction (8) because N_2O was not recovered at any flow rate of NO. The failure to find N_2O among the products of the NO reaction cannot be attributed to destruction by atomic nitrogen or oxygen since Kistiakowsky and Volpi (91) found no evidence that N_2O reacted with either oxygen or nitrogen atoms at temperatures up to 200°C. Kaufman (105) has confirmed that N_2O is not destroyed by active nitrogen and a brief series of experiments at 300°C during the present study showed that less than 5% of the N_2O reacted.

The difference between the amount of hydrogen cyanide produced from ethylene and the amount of nitric oxide destroyed could conceivably have been due to some processes other than reaction (8).

One possibility that might be suggested is a chain mechanism involving reaction of the collision complex of NO and a nitrogen atom

$$N + NO \longrightarrow NNO \qquad (12)$$

$$NO + NNO \longrightarrow N_2 + O_2 + N \qquad (13)$$

$$NNO \longrightarrow N_2 + O \qquad (14)$$

The collision complex would probably be very similar to a highly excited N_2O molecule with energy available to it to the extent of 134 kcal. minus its heat of formation. Hence it should decompose quite easily by reaction (14) which is only 39 kcal. endothermic for a ground state N_2O molecule. An appreciable lifetime for the complex would therefore appear to be very unlikely. Reactions (12) and (13) may be regarded as equivalent to the exothermic over-all reaction

$$2NO \longrightarrow N_2 + O_2 + 43 \text{ kcal}$$

and therefore superficially plausible. However, such a mechanism cannot be reconciled with the observed plateau value of NO destroyed, independently of NO flow rate since the rates of disappearance of the complex by the chain carrying step, reaction (13), and by the chain breaking step, reaction (14), are obviously different functions of the NO concentration.

Another possible alternative to reaction (8) to explain the difference between the amount of hydrogen cyanide produced from ethylene and the amount of NO decomposed might be an energy transfer from "hot" oxygen atoms to nitric oxide by the mechanism

$$N + NO \longrightarrow N_2 + O^* \qquad (8)$$

$$O^* + NO \longrightarrow NO^* + O \qquad (16)$$

$$NO^* + NO \longrightarrow N_2 + O_2 \qquad (17)$$

For reaction (17) to be thermoneutral, the NO^* molecule would require 43 kcal. of excess energy. Sufficient energy is available from reaction (8) to produce an oxygen atom in the excited ^1D state which lies approximately 45 kcal. above the ground state. Actually, this reaction is spin forbidden and the energy is more likely to exist as translational energy of a normal ^3P atom$, in which case equipartition of momentum would leave some 47.7 kcal. with the oxygen atom. Destruction of NO by energy rich atoms, especially if their energy is translational, should become less important at higher pressures where the likelihood of collisional deactivation is increased. Since the ratio of NO destroyed to hydrogen cyanide formed was, in fact, found to increase with pressure, it does not appear that "hot" oxygen atoms can be responsible for the relatively greater extent of reaction with NO.

A difference between the maximal amount of hydrogen cyanide produced from ethylene and the amount of NO decomposed would be readily explained if, in addition to atomic nitrogen with which both ethylene and NO can react, there is a second species present in active nitrogen which is capable of decomposing NO but is not capable of producing hydrogen cyanide from ethylene. If, as suggested previously (82), this second species is an excited molecule of sufficient energy, destruction of NO might occur by

$$N_2^* + NO \longrightarrow N_2 + N + O \qquad (18)$$

Only two species of excited molecules have lifetimes sufficiently long to allow the accumulation of a significant concentration; these are

molecules in the $A^3\Sigma_u^+$ state, the end product of the yellow afterglow, and vibrationally excited ground state molecules (64).

Decomposition of NO by electronically excited nitrogen molecules seems quite plausible. Vibrational levels of the A state are known up to $\nu = 16$. Any of the levels with $\nu > 2$ will have sufficient energy (6.49 e.v.) to cause dissociation of NO. Since molecules in the A state are formed by radiation from the B state, the population distribution will be weighted in favour of the lower vibrational levels of the A state. This in turn will favour successful collisions of the second kind with NO since the dissociation energy of NO is very nearly the same of the energy of the A state molecules (107, 108). It may be noted that, if the N_2 is in the $A^3\Sigma_u^+$ state, reaction (18) conserves spin.

The radiative half life of the A state is now recognized (60) to be of the order of 0.1 sec., which is approximately equal to the time required for the active nitrogen to travel the length of the long reaction tube and considerably longer than the 0.02 sec. needed to pass from the discharge tube to the reaction vessel when the long reaction tube is not used. The rate constant for the gas phase (homogeneous) recombination of nitrogen atoms determined by Berkowitz et al. (56), and confirmed by a different method in this laboratory (108), leads to a concentration of molecules in the A state of the right order of magnitude to account for the excess of NO destroyed over HCN formed from ethylene under conditions of complete reaction. Since the extent of dissociation in the discharge

tube was not known, a rigorous treatment is unfortunately not possible, it is also not known how effective normal nitrogen molecules are in the deactivation of the triplet state.

Ground state vibrationally excited nitrogen molecules could be produced in considerable quantities in the discharge tube by collisions of the second kind, as well as by the crossing-over of $A^3\Sigma_u^+$ molecules into the adjacent levels of the ground state in the perturbing field of a normal molecule. Vibrational levels of nitrogen molecules in the $X^1\Sigma_g^+$ state have been observed up to $\nu = 27$ (110). The 27th level lies 6.6 e.v. (152 kcal.) above ground and the 26th level at 6.33 e.v. Since the bond strength of nitric oxide D(NO), is 6.49 e.v. (149 kcal.) only those molecules in the highest observed vibrational level would appear to have sufficient energy to cause the dissociation of NO.

Assuming that the half-life of a vibrational level of ground state nitrogen is of the order of 10^6 collisions (66) and knowing that a molecule will suffer some 10^7 collisions per second under the experimental conditions, a half-life for a given level of 0.1 seconds as obtained. This value is the same as the probable half-life of the electronically excited molecule so that vibrationally excited nitrogen is equally probable by this criterion.

It does not seem possible, from the present study, to come to any definite conclusion about the relative importance that electronically

excited and ground state vibrationally excited molecules might have in decomposing NO. The experiments which were made with different power inputs to the discharge showed that the ratio of nitric oxide destroyed to hydrogen cyanide produced from ethylene was essentially constant. This could constitute an argument against electronically excited molecules as the second active species. The formation of molecules in the A state is due to the recombination of atoms and therefore dependent on the second power of the atom concentration. Since lower concentrations of these at the reaction vessel presumably correspond to lower concentrations in the discharge tube, the rate of formation of A state molecules should decrease more sharply with decrease of atom concentration than the loss of activity by first order surface recombination of atoms on the wall.* It is true however that homogeneous recombination will be most important during the very short time interval immediately following the discharge so that the ratio, which was determined after a time much larger than this interval, would not be sufficiently sensitive to rule out electronically excited molecules as the second species.

If the results with nitric oxide seem to favour vibrationally excited molecules as a second possible species in active nitrogen, the behaviour with ammonia suggests that electronically excited molecules are more influential. It will be recalled that the reaction of active nitrogen with ammonia resulted in about 20% as much destruction of ammonia as hydrogen cyanide production from ethylene under optimal

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* The partial pressure of atomic nitrogen was not sufficiently low at any time that the surface recombination might also become second order.

conditions. If the destruction of ammonia is attributed to excited molecules only, its extent ought to correspond to one half the difference between the active nitrogen concentration indicated by NO destruction and hydrogen cyanide formation respectively, since the dissociation of each NO molecule would involve the formation of a nitrogen atom which would further react with NO by reaction (8). This was true at the first reactant inlet but farther down the reaction tube, the agreement was less good. Uncertainties in the determination of such small quantities by difference were probably sufficient to account for the discrepancy.

The lower bond strength of the hydrogens in ammonia would allow reaction of vibrationally excited ground state molecules with $v < 27$. This should tend to increase the amount of ammonia destroyed and make it larger than twice the difference between NO destroyed and hydrogen cyanide produced. Since this was not observed, electronically rather than vibrationally excited molecules appear to be the preferred possible second species.

THE NITROGEN DIOXIDE REACTION

The reaction of active nitrogen with nitrogen dioxide was found to lead to the formation of a considerable quantity of nitrous oxide. This was almost certainly formed by the reaction

$$N + NO_2 \longrightarrow N_2O + O + 42 \text{ kcal.} \qquad (19)$$

Since N_2O is known to be almost completely unreactive toward both active nitrogen and atomic oxygen, the amount of it found among the reaction

products may safely be considered a true measure of the extent to which reaction (19) occurs.

When NO_2 was introduced into active nitrogen at flow rates less than 14.0 micro-moles/sec., no oxide of nitrogen other than N_2O was recovered. At flow rates larger than 14.0 micro-moles/sec. NO and NO_2 were also found among the products. However the N_2O , at all times, amounted to only a fraction of the NO_2 which was not recovered as either NO or NO_2. A portion of the NO_2 must therefore have been converted into non-condensible products. This would seem to indicate that, together with reaction (19), there occurred the over-all reaction represented by

$$N + NO_2 \longrightarrow N_2 + O_2 + 122 \text{ kcal.} \qquad (20)$$

Reaction (20) might take place by a more complicated mechanism than that indicated by the overall equation. One possibility is the sequence

$$O + NO_2 \longrightarrow NO + O_2 + 47 \text{ kcal.} \qquad (21)$$

$$N + NO \longrightarrow N_2 + O + 75 \text{ kcal.} \qquad (8)$$

It is not possible to determine from the products whether this is the actual mechanism. However, this scheme would seem to imply that competition for active nitrogen occurs between reactions (19) and (8), so that in the presence of a large excess of NO_2, reaction (19) ought to be favoured. Actually the yield of N_2O reached a plateau value almost as soon as the flow rate of NO_2 was sufficient to destroy all active

nitrogen. This suggests that no competition for active nitrogen did occur between reaction (19) and a reaction such as (8) involving a substance other than NO_2. It must be admitted though, that this is not a very sensitive criterion since only about one third of the NO_2 which reacts is converted to N_2O.

Examination of the data for production of atomic oxygen in the system reveals that reactions (19) and (20) are not adequate to explain all the experimental results. The green afterglow from excited NO_2 molecules, formed by the reaction of atomic oxygen with nitric oxide

$$O + NO \longrightarrow NO_2^* \qquad (23)$$

became visible when the flow rate of NO_2 exceeded 14 micro-moles/sec. and persisted the length of the reaction tube until quenched by either a silver wire or a cold trap. When the flow rate of NO_2 was further increased to 25 micro-moles/sec., this green glow was rather suddenly reduced to only a thin "layer". This may be taken to mean (94) that at this point all, or nearly all oxygen atoms had been consumed by the reaction

$$O + NO_2 \longrightarrow NO + O_2 \qquad (21)$$

which, under the experimental conditions is very much faster (93) than the three body process

$$O + NO + M \longrightarrow NO_2 + M \qquad (24)$$

Since no NO or NO_2 were recovered at a flow rate of NO_2 smaller than 14.0 micro-moles/sec., it may be concluded that the minimum flow rate of

atomic oxygen was equal to the difference of 11 micro-moles/sec., between the flow rate of NO_2 where the green glow first appeared and where it disappeared.* A flow rate of atomic oxygen of 11 micro-moles/sec. can evidently not be accounted for by a mechanism involving only reactions (19) and (20) since the maximum number of oxygen atoms produced in this manner cannot exceed the flow rate of N_2O which was never larger than 4.9 micro-moles/sec.

It becomes necessary therefore to postulate another reaction to produce oxygen atoms. The most plausible one would seem to be

$$N + NO_2 \longrightarrow N_2 + 2O + 4\ \text{kcal.} \qquad (25)$$

If all the NO_2 destroyed by active nitrogen (14.0 micro-moles/sec.), apart from that converted to N_2O (4.9 micro-moles/sec.), were to react by (25), an atomic oxygen flow rate of at least 18 micro-moles/sec. would result. Since this is considerably in excess of the value of 11 micro-moles/sec. indicated by "titration" to the disappearance of the green glow, it would be necessary for reaction (25) to occur to only a limited extent of about 3 micro-moles/sec. destruction of NO_2.

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* At first glance, the above argument might seem to be invalidated by the fact that some NO_2 was recovered before the NO_2 flow rate reached the value of 25 micro-moles/sec. However, the presence of NO_2 may be accounted for by the reaction of molecular oxygen with nitric oxide on the surface of the cold trap. This was experimentally verified by passing molecular oxygen and NO through a trap at -210°C. The reaction must occur in the cold trap because the gas phase oxidation of NO, as calculated from the rate constants of Bodenstein (109), is too slow to play an important part.

There remains to be considered the formation of NO since it was found among the reaction products in considerable quantity, A plot of the sum of NO and NO_2 recovered versus flow rate of NO_2 proved to be a straight line with a slope of unity, which extrapolated to 14.0 micro-moles/sec. of NO_2 at zero recovery of these oxides. The most plausible interpretation of this would seem to be that, up to this flow rate of 14 micro-moles/sec., all the NO_2 reacts with active nitrogen and beyond this all the excess is recovered with a portion converted to NO, presumably by reaction with oxygen atoms generated in the active nitrogen reaction.

According to this interpretation, the recovery of NO should be linear in NO_2 flow rate, with a slope of unity, until it reaches a value equal to the flow rate of oxygen atoms. Beyond this point the amount of NO recovered should be a constant. In fact, recovery of NO_2 started simultaneously with recovery of NO and the amount of the latter in the reaction products increased more slowly than this to approach a limiting value of approximately 14 micro-moles/sec. at high flow rates of NO_2. This behaviour may be explained if we take into account reaction between molecular oxygen and NO on the walls of the trap,

$$2NO + O_2 \longrightarrow 2NO_2 \text{ or } N_2O_4 \qquad (26)$$

in competition with the reaction (probably on the wall also)

$$NO + NO_2 \longrightarrow N_2O_3 \qquad (27)$$

The formation of N_2O_3 was evident from its dark blue colour which could

be clearly discerned in the trap. The fact that the ratio of NO to NO_2 recovered proved to be less accurately reproducible than the sum of the two, would seem to be consistent with the proposed heterogeneous reactions.

The amount of NO recovered appeared to extrapolate to a limiting value of approximately 14 micro-moles/sec. If this much NO is to be attributed to the reaction of oxygen atoms with NO_2 by reaction (21), the flow rate of atomic oxygen must also have been 14 micro-moles/sec. This is appreciably in excess of the value of 11 micro-moles/sec. determined by "titration" to the disappearance of the green afterglow. It is possible however, that only 85% of the true atomic oxygen flow rate is given by this method, in which case the oxygen atom flow rate of 14 micro-moles/sec., derived from the amount of NO formed, would come within the experimental error (p. 18).

The amount of NO_2 destroyed by active nitrogen was 14.0 micro-moles/sec.* whereas the amount of NO destroyed under identical conditions was 18.7 micro-moles/sec. If the reaction

$$N + NO_2 \longrightarrow 2\,NO \qquad (28)$$

had consumed 2.35 of the 14.0 micro-moles/sec. of NO_2, thereby forming 4.7 micro-moles/sec. of NO which was also destroyed by active nitrogen, the total destruction of NO_2 and NO would have been the same as that observed in the NO reaction. However, it would be remarkably fortuitous that reaction (28) should have occurred to just the extent necessary

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* It will be recalled that only N_2O was recovered at NO_2 flow rates less than 14.0 micro-moles/sec.

for the amount of NO_2 destroyed to coincide almost exactly with the amount of hydrogen cyanide formed from ethylene under optimal conditions, 13.9 micro-moles/sec. While reaction (28) cannot be ruled out on this ground alone, an alternative and perhaps more attractive possibility is that NO_2 is partially decomposed by excited nitrogen molecules according to the reaction

$$N_2^* + NO_2 \longrightarrow N_2 + NO + O \qquad (29)$$

This would be more in line with the earlier discussion where it was assumed that the difference between the hydrogen cyanide formed from ethylene and the amount of NO destroyed by the same concentration of active nitrogen was due to destruction of some NO by excited nitrogen molecules which were not capable of forming hydrogen cyanide from ethylene. Reaction (29) requires only some 71 kcal. of excess energy on the part of the nitrogen molecules to be thermoneutral, a condition they should easily meet if they are capable of dissociating the 149 kcal. bond in NO. According to the recent observations of Kaufman (105), they might also be quenched to a certain extent by the N_2O which is formed in the reaction of NO_2 with nitrogen atoms. It is possible, especially in the region where the NO_2 is only in slight excess over the nitrogen atoms, that some decomposition of NO occurs by energy rich nitrogen molecules but the extent of such decomposition might well be within the limits of experimental error.

The results of this study of the active nitrogen - NO_2 reaction differ, in a number of ways, from those reported by Kistiakowsky and Volpi (91). Perhaps the most obvious point of difference

is the much larger yield of N_2O that was obtained during the present work. Part of this difference is probably due to the difficulty, mentionned by these authors, of obtaining reliable mass spectrometer data in the presence of NO_2 (see also 97). An additional complication might have been introduced by the uncertain contribution of CO_2 to the mass 44 peak. In an earlier paper (56), this apparently led to the erroneous identification of N_2O as a major product of the reaction between active nitrogen and NO. Since no measurement of either atomic oxygen or NO was possible with the mass spectrometer, a more detailed comparison is probably not warranted. Also, the present study was made with a concentration of active nitrogen almost ten times that used by Kistiakowsky and Volpi, and this might have contributed to differences in the results of the two investigations.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The reaction of active nitrogen with nitric oxide was studied over a wide range of flow rates of both nitric oxide and active nitrogen. It is suggested that nitric oxide was destroyed principally by the reaction

$$N + NO \longrightarrow N_2 + O$$

Nitrous oxide was not recovered among the reaction products which is considered evidence that the spin forbidden reaction

$$N + NO \longrightarrow N_2O$$

effectively did not occur.

2. The amount of nitric oxide destroyed by active nitrogen was compared with the maximal amount of hydrogen cyanide formed by reaction with ethylene under identical conditions at each of a number of flow rates of active nitrogen. These were obtained by varying the power input to the discharge tube over a range of 16 to 1 with a resulting range of active nitrogen flow rates of 10 to 1. The amount of nitric oxide destroyed was found to be larger than the amount of hydrogen cyanide formed by a factor of 1.5 which remained essentially constant independently of concentration of active nitrogen.

3. The amounts of nitric oxide and ammonia destroyed by active nitrogen were compared with the maximal amount of hydrogen cyanide formed from ethylene at different distances from the discharge tube. Slightly

more than half the active nitrogen decayed over the total distance involved. The ratio of nitric oxide destroyed to hydrogen cyanide formed was approximately 1.4 and varied but little with distance. The amount of ammonia destroyed equalled about one sixth of the hydrogen cyanide yield. The shape of the active nitrogen concentration versus distance curve indicated by these three reactants proved to be almost identical.

4. The ratio of nitric oxide destroyed to hydrogen cyanide formed was determined at three points over a pressure range of 4 to 1. The ratio increased slowly with pressure.

5. The reaction of active nitrogen with ethylene was reviewed in detail on the basis of this and previous work. It is concluded that the maximal hydrogen cyanide yield from this reaction is a measure of the concentration of nitrogen atoms in active nitrogen.

6. The reaction of active nitrogen with nitric oxide was reviewed and various explanations examined that might account for the excess of nitric oxide destroyed over hydrogen cyanide. It is proposed that the difference is due to the reaction of excited nitrogen molecules by

$$N_2^* + NO \longrightarrow N_2 + N + O$$

Arguments are advanced to show that both nitrogen molecules in the $A^3\Sigma_u^+$ state and vibrationally excited molecules in the ground state with $\nu \geq 27$ could be the second active species and that this second species is probably responsible for the destruction of ammonia

when ammonia is introduced into active nitrogen.

7. The reaction of active nitrogen with nitrogen dioxide was studied over a range of NO_2 flow rates. The presence of nitrous oxide among the products is attributed to the reaction

$$N + NO_2 \longrightarrow N_2O + O$$

The reactions

$$N + NO_2 \longrightarrow N_2 + O_2$$

$$N + NO_2 \longrightarrow N_2 + 2O$$

are proposed to account for the loss of a fraction of the NO_2 which was not recovered as any oxide of nitrogen, and to explain an oxygen atom flow rate in excess of the flow rate of N_2O. It is suggested that formation of nitric oxide, which was also found among the products, is due to the oxygen atom reaction

$$O + NO_2 \longrightarrow NO + O_2$$

It is possible that the reaction

$$N + NO_2 \longrightarrow 2\,NO$$

occurred, but analysis of the results indicates that a more probable reaction is partial decomposition of nitrogen dioxide by excited nitrogen molecules

$$N_2^* + NO_2 \longrightarrow N_2 + NO + O$$

8. On the basis of the band spectra emitted when NO and NO_2 were present in lesser and greater amounts than active nitrogen, reaction times were estimated and lower limits proposed for the second order rate constants of the reactions of NO and NO_2 with active nitrogen.

APPENDIX

TABLE X

STANDARD HEATS OF FORMATION OF GASEOUS SUBSTANCES AT 25°C

Substance	ΔH_f° kcal/mole	Reference
H	52.09	(i)
N	112.5	(48)
O	59.16	(i)
NO	21.60	(i)
NO_2	8.09	(i)
N_2O	19.49	(i)
NH_3	11.04	(i)
NH_2	41	(ii)
NH	77	(ii)

(i) Selected Values of Chemical Thermodynamic Properties Circular 500 of the National Bureau of Standards (1952)

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