THE REACTION OF ACTIVE NITROGEN WITH OXYGEN

THE REACTION OF ACTIVE NITROGEN WITH OXYGEN

by

Athanasios S. Vlastaras

B.Sc. (Athens)

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
Professor C.A. Winkler

Department of Chemistry,
McGill University,
Montreal, Canada.

November, 1966.

TO MY PARENTS

ACKNOWLEDGEMENTS

The author wishes to express his appreciation

to

the National Research Council of Canada for financial assistance in the form of a Studentship during the academic year 1965-66;

to

the Department of Chemistry, McGill University, for Demonstratorships held during the academic years 1963-64, 1964-65, 1965-66.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table Page

INTRODUCTION

ACTIVE NITROGEN

When a stream of ordinary molecular nitrogen, itself a relatively inert gas, is subjected to an electric discharge a bright golden-yellow glow may be observed downstream from the discharge. This glow, the so-called nitrogen afterglow, may persist for a considerable time after the discharge is switched off. It was first observed by Warburg (1) in 1884, and was studied spectroscopically, in 1900, by Lewis (2). He was able to identify the emission spectrum as that of nitrogen. Much more extensive studies were made by Strutt (later,Lord Rayleigh) during the period from 1911 until his death in 1947. Of particular interest were his experiments that demonstrated the great chemical reactivity of the glowing gas, as a consequence of which he referred to it as 'active nitrogen'. It is interesting to note that he attributed many of its properties to the presence of atomic nitrogen (3). The yellow glow has since been known as the 'Lewis-Rayleigh' afterglow.

Since the discovery of active nitrogen, numerous experimental studies have been made, to explain the mechanism of the afterglow and to elucidate the nature of the active species in active nitrogen. These studies prior to 1945 are reviewed briefly in a book by Mitra (4), entitled 'Active Nitrogen - A New Theory'. Reviews of more recent studies have also been made available by Jennings and Linnett (5), Edwards (6), and

Mannella (7). The remarks that follow will therefore not attempt anything in the nature of a comprehensive review, but will be limited, essentially, to the important points that are necessary for discussing the work of the present investigation.

Active nitrogen is generally produced by the passage of an electrical discharge through nitrogen at low pressures. The discharge may be condensed (intermittent) between electrodes, or of the electrodeless (microwave) type, first used by Burke (8). An arc discharge may also be used,at pressures as high as 20 cm Hg (9). Active nitrogen has also been produced by an electrical discharge through ammonia or nitric oxide (10), and by bombardment of nitrogen with electrons of energy greater than 16.3 e.v. (11).

The purity of the nitrogen is important. Absolutely pure nitrogen fails to give the afterglow, as suggested by Comte (12), and confirmed by Lewis (13), Rayleigh (14) and recently by Anderson (15). The glow is enhanced when foreign gases are added (3), in trace amounts insufficient for the spectra of the gases to appear in that of the glow (16).

When active nitrogen is passed between electrodes, it shows relatively high electrical conductivity (3). This conductivity was attributed, in the past, to the presence of positive ions in the gas phase (17). Benson (18) has recently found that the charged particles in active nitrogen were mainly electrons, at a concentration less than 10^{-6} that of the chemically active species. He also pointed out that active nitrogen did not show any response to magnetic fields, and removal of ions from active nitrogen had no effect on the glow.

The introduction of foreign substances into a stream of active nitrogen usually results in a flame at the point of mixing. Certain characteristics of this flame, such as length and colour, depend upon the nature and concentration of the added substance. The spectra of these flames are due either to the unchanged substances, excited by energy transfer from active nitrogen, or to excited species formed in chemical reactions with active nitrogen. Nitrides are formed in the reaction between active nitrogen and metallic vapours, while hydrogen cyanide is the main product with hydrocarbons and their derivatives (3,19).

The discharged nitrogen is characterized by a pink glow in the discharge region. The N_2 first positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$), N_2 second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$), and N_2^+ first negative ($B^2\Sigma_u^- \rightarrow X^2\Sigma_g^+$) bands, are emitted. The 'Lewis-Rayleigh' afterglow emits only the N_2 first positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) bands (20,21,22,23,24). From the terminal A state of the first positive emission, the nitrogen molecule falls to the ground $X^1\Sigma_g^+$ state with emission of the 'forbidden' Vegard-Kaplan bands. (See Fig. 1)

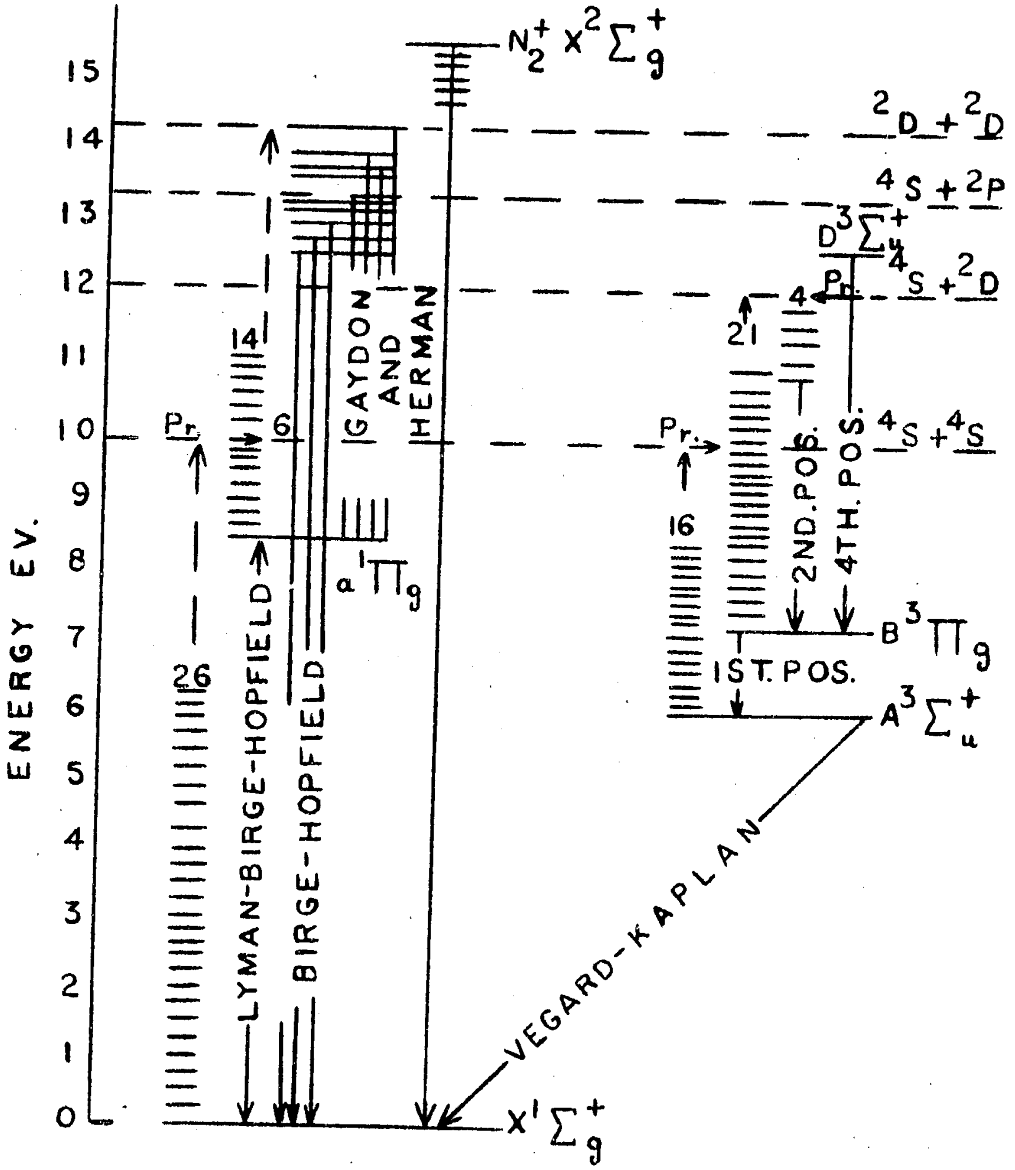
The strongest transitions of the first positive system are those from the 12, 11, 10, 7 and 6th vibrational levels of the $B^3\Pi_g$ state to the 9, 8, 7, 4 and 3rd vibrational levels of the $A^3\Sigma_u^+$ state (20,21,25). Kistiakowsky and Warneck (26)

Figure 1

ENERGY LEVEL DIAGRAM OF THE NITROGEN MOLECULE

The longer horizontal lines indicate the
electronic states, and the shorter
horizontal lines indicate the
vibrational levels

(Reproduced from reference 63)



ENERGY LEVEL DIAGRAM OF THE N_2 MOLECULE proposed that the weaker transitions do not belong to the first positive system.

The decay of the afterglow was found to be proportional to the square of the ground-state nitrogen atom concentration, under a variety of conditions (27). By experiments that involved dilution, compression and expansion of active nitrogen, Rayleigh (28) showed that the process was termolecular, being second order in the active species and first order in molecular nitrogen, which acts as a third body in the process. He also suggested that the reaction responsible for the afterglow might have a negative temperature coefficient, since the intensity of the glow decreased with an increase in temperature.

The energy content of active nitrogen has been variously estimated from 2 to 12.9 e.v./mole of total nitrogen. The value of 2 e.v. was suggested by Willey and Rideal (29), based on calorimetric data for the reactions of nitric oxide and air with active nitrogen. On the other hand, experiments on the excitation of mercury lines by active nitrogen yielded a value of 9.5 e.v. (30,31). When metal foils were exposed to active nitrogen, the energy liberated appeared to correspond to values that ranged from 4.32 to 12.9 e.v./mole of total nitrogen (32). However, Benson (18) obtained a value of only 0.027 e.v./mole of total nitrogen, from careful calorimetric experiments, and he has ascribed the discrepancy to the bombardment of the foils by electrons from the discharge.

The bond dissociation energy of the ground-state nitrogen molecule, although a most important quantity, was not known with certainty for many years. The suggested values were generally in the neighbourhood of either 7.373 or 9.764 e.v. The first value was proposed by Herzberg (33), based on the pre-dissociation of nitrogen; he pointed out, however, that the possibility $D(N_2) \doteq 9.756$ e.v. was not conclusively eliminated. Gaydon (34) concluded that the pre-dissociation in the $B^3\Pi_g$ state was possibly the result of recombination of $N(^4S)$ atoms through an intermediate $^5\Sigma_g^+$ state. This explanation gave the second value, 9.764 e.v., for the dissociation energy (34,35). Experiments on detonation velocities in nitrogen (36), thermal decomposition of nitrogen (37), and dissociation of nitrogen by monoenergetic electrons (38), have established the correctness of the higher value, and the value now accepted for $D(N_2)$ is 9.756 e.v. or 225 Kcal, i.e. 112.5 Kcal/mole for the heat of formation for $N(^4S)$ atoms.

THEORIES OF THE LEWIS-RAYLEIGH AFTERGLOW

Attempts to explain the production and behaviour of the 'Lewis-Rayleigh' afterglow have been made from the early days of its discovery until today. The uncertainty about the energy content of active nitrogen, and the dissociation energy of the nitrogen molecule, has led to controversial postulates about the species that might be present, hence about the mechanism by which the afterglow might be developed. When both the energy content and dissociation energy were finally established, and improved techniques were available for identifying the species present in active nitrogen, the mechanism of the afterglow became more detailed, although not completely resolved.

Rayleigh (Strutt) (3) suggested that the properties of active nitrogen were due mainly to the presence of nitrogen atoms, an assumption which was supported later by the experimental production of atomic hydrogen (39,40). On this basis Sponer (41) proposed, in the earliest theory of the afterglow, that it resulted from a two-step mechanism,

$$N + N + M \rightarrow N_2^* + M$$

$$N_2^* \rightarrow N_2 + h\nu \quad \text{(afterglow)}.$$

The suggested third-order kinetics agreed with the experimental behaviour and also explained the long life of the afterglow. However, this theory fails to account for the selective enhancement of certain transitions in the spectrum of the afterglow, and for the electrical properties of active nitrogen.

Cario and Kaplan (42) proposed the presence of metastable atoms and metastable molecules in active nitrogen. They assumed production of vibrationally excited molecules in the B state, by collisions of the second kind, which produced the afterglow by the following mechanism:

$$N(^2P) + N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi_g) + N(^4S)$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \quad \text{(afterglow)}.$$

Such a mechanism was able to explain the selective enhancement of transitions from the 12th and lower vibrational levels of the B state, and was favoured, at the time, over the atomic theory. It gained some experimental support from a Stern-Gerlach experiment (43) in which a beam of active nitrogen and a silver nitrate target were used. However, opposed to the theory were the later experiments of Worley (44), who observed no Vegard-Kaplan bands corresponding to the transition $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$, which indicated a very low concentration of nitrogen molecules in the A state. Also, Herbert et al. (45) showed that an upper limit for the concentration of metastable, ^2P, atoms did not exceed 10^{-4} per cent.

Cario (46) modified the original theory and suggested that metastable atoms and metastable molecules were not produced in the discharge region, but resulted from triple collisions between $N(^4S)$ atoms and ordinary nitrogen molecules.

Largely on the basis of Rayleigh's (32) metal foil experiments, Mitra (4) proposed, in 1945, that active nitrogen was a mixture of N_2^+ ions and electrons, which gave rise to the afterglow by the sequence:

$$N_2^+ + e + N_2 \rightarrow N_2(B^3\Pi_g) + N_2(A^3\Sigma_u^+)$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \quad \text{(afterglow)}.$$

The theory readily explains the electrical properties of active nitrogen, the long life of the afterglow, and the kinetics of its decay. However, Gaydon (35) was opposed to Mitra's theory, on the grounds that the heating effects observed by Rayleigh were probably due to cathode rays from the discharge region, a point which, as indicated previously, was subsequently proven experimentally by Benson (18). He observed that, when the electrons were removed from the gas stream, the heating effects were much reduced. Experimental evidence against the theory was also obtained by Worley (44), who failed to observe the (0,0) bands of N_2^+ in absorption with a path length of 13 m. Mitra (47) finally conceded that the theory was untenable.

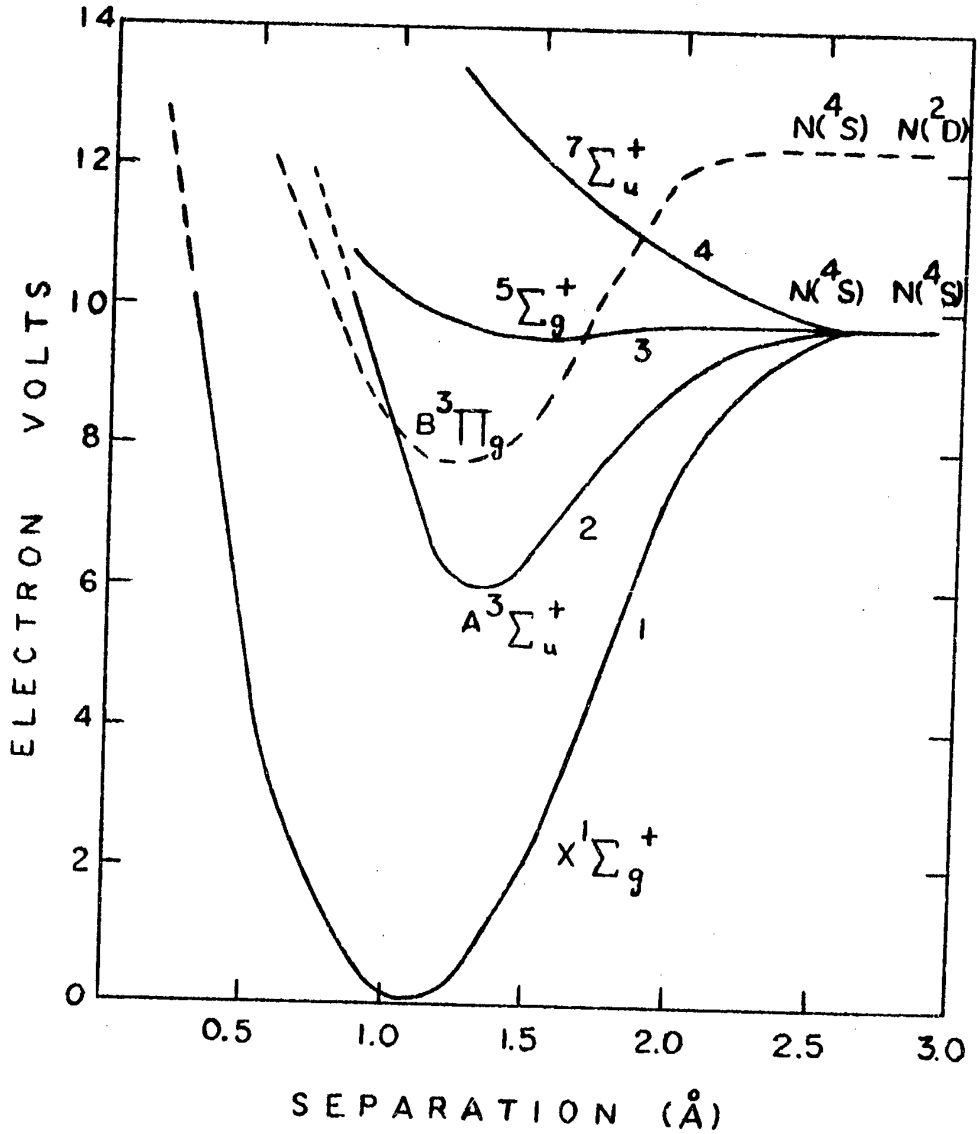
The suggestion that pre-association of nitrogen atoms may occur through a quintet state provides a basis for explaining most of the experimental observations on the behaviour of the afterglow. The ground state nitrogen atom has the electronic configuration $1s^2\ 2s^2\ 2p_x\ 2p_y\ 2p_z$, with three unpaired p electrons of parallel spin. When two atoms of the above configuration come together, molecules are formed in different states, depending upon the pairing of the six electrons. They can approach each other along four different potential energy curves, labelled 1, 2, 3 and 4 in Fig. 2, corresponding to the pairing of 6, 4, 2 and 0 electrons, Depending upon the paths, the molecular states formed are designated $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$ and $^7\Sigma_u^+$, and their formation probability is as the ratio of their multiplicities, 1:3:5:7.

The molecules so formed must be stabilized by a collision with a third body to remove the excess energy. If

Figure 2

POTENTIAL ENERGY CURVES FOR SOME STATES
OF THE NITROGEN MOLECULE

(Reproduced from reference 5)



14
12
10
8
6
4
2
0
ELECTRON VOLTS
0.5
1.0
1.5
2.0
2.5
3.0
SEPARATION (Å)
$^7\Sigma_u^+$
N(^{4}S) N(^{2}D)
4
$^5\Sigma_g^+$
N(^{4}S) N(^{4}S)
3
$B^3\Pi_g$
2
$A^3\Sigma_u^+$
1
$X^1\Sigma_g^+$

the atoms follow path 1 or 2 (Fig. 2), the resulting molecule will be in the $X^1\Sigma_g^+$ ground state or $A^3\Sigma_u^+$ first excited state, respectively. For path 4, the molecule will be unstable, even in the presence of a third body, since no bond is formed (the $^7\Sigma_u^+$ potential energy curve is repulsive).

The most interesting possibility is that the atoms might follow path 3, which leads to a weakly bound nitrogen molecule in the $^5\Sigma_g^+$ state. The potential energy curve of this state crosses that of the B state. This was first noted by Gaydon (34), to explain the pre-dissociation observed in the first positive system of nitrogen due to the transition $B^3\Pi \rightarrow A^3\Sigma$. He assumed that molecules in the levels v' = 13-16 of the B state can undergo a collision-induced radiationless transition to the $^5\Sigma_g^+$ state, which then dissociates into ^4S atoms. The reverse of this process produces molecules in the B state from ^4S atoms. In the afterglow, two ^4S atoms collide on the $^5\Sigma_g^+$ potential energy curve, after which a collision with a third body induces a pre-association into the 12th vibrational level of the B state (27,35).

Kistiakowsky and Warneck (26) used an isotopic labelling technique to obtain proof of a two-step mechanism previously proposed by Brook (48), and developed by Berkowitz _et al_. (27),

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

$$N_2(^5\Sigma_g^+) + M \rightarrow N_2(B^3\Pi_g) + M.$$

The distribution curve for light emission from various vibrational levels of the $B^3\Pi_g$ state showed that the above mechanism was valid only for higher vibrational levels, $v' = 8\text{-}12$, while the transitions from lower vibrational levels were due to some other mechanism. They identified three bands which did not fit into the first positive system. A new state, 'Y', was proposed, as the initial state for the new bands, which was itself populated from the $^5\Sigma_g^+$ state, through a collision-induced transition, in competition with the transition to the $B^3\Pi_g$ state.

Peyron and Broida (49), working at very low temperatures, were able to identify the $^5\Sigma_g^+$ state, which gave support to the pre-association theory. They calculated $D_o\ N_2(^5\Sigma_g^+) = 0.13$ e.v., based on $D_o\ N_2 = 9.76$ e.v.

Le Blanc _et al_. (50) found a new band system, by passing a discharge through mixtures that contained 5-10% nitrogen with 95-90% argon, with the subsequent afterglow tube cooled with liquid nitrogen. They proposed the $^3\Delta_u$ state as the upper state, while the lower state of the system was thought to be the B state. The $^3\Delta_u$ state can be produced by a collision-induced radiationless transition from the $^5\Sigma_g^+$ state.

Gaydon (35) has observed, in the Lyman-Birge-Hopfield bands of the afterglow, a forbidden pre-dissociation in the $v' = 6$ level of the $\alpha^1\Pi_g$ state. He suggested that this is due to the process $N_2(\alpha^1\Pi_g) \rightarrow N_2(^5\Sigma_g^+) \rightarrow N(^4S) + N(^4S)$. The reverse of this process can give rise to the Lyman-Birge-Hopfield bands in emission.

The pre-association theory has been expanded by Bayes and Kistiakowsky (51), in an effort to explain their own experimental results, as well as the previously known properties of the afterglow. The proposed mechanism can be summarized as follows:

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

$$N_2(^5\Sigma_g^+) \rightarrow N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$$

(first positive system)

$$\rightarrow N_2(Y^3\Sigma_u^-) \rightarrow N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$$

(proposed new bands)

$$\rightarrow N_2(^3\Delta_u) \rightarrow N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$$

(proposed new bands)

$$\rightarrow N_2(\alpha^1\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + h\nu$$

(Lyman-Birge-Hopfield bands).

The Bayes-Kistiakowsky mechanism cannot explain some parts of the afterglow spectrum, both at high and very low pressures. However, it has proved to be a useful basis for suggesting both theoretical and experimental investigations.

REACTIVE SPECIES IN ACTIVE NITROGEN

Various species have been proposed to explain the chemical reactivity of active nitrogen. There is no doubt that, of the various species present, nitrogen atoms in the ^4S

ground state are of major importance. On the other hand, there is experimental evidence that part of the reactivity may be attributed to excited nitrogen molecules.

The presence of atoms in active nitrogen, suggested initially by Strutt (3), was demonstrated experimentally by Wrede (53). He was able to detect a pressure difference ascribable to differential diffusion of atoms, relative to molecules, through a pin-hole (the so-called Wrede gauge). As outlined previously, a Stern-Gerlach experiment suggested that the atoms were excited to the $^2P_{1/2}$ state. However, failure to detect absorption in the vacuum ultraviolet, where both ^2P and ^2D atoms would absorb, indicated that the concentration of excited atoms was only 1/6000 the total atom concentration in active nitrogen. Other experiments by Tanaka <u>et al</u>. (54) gave the total concentration of ^2P and ^2D atoms as 1/500 the concentration of $N(^4S)$ atoms. Emission corresponding to the transition $^2D \rightarrow {}^4S$ has been observed by Broida and co-workers (55,56) from solid products condensed at $4.2^\circ K$ from the nitrogen afterglow, but they did not estimate the ^2D atom concentration.*

Direct experimental evidence for ground state atoms in active nitrogen has been obtained from the para-magnetic resonance spectrum of active nitrogen (57), and from mass spectrometric studies on active nitrogen (58). An appearance potential of 14.7 ± 0.2 e.v. agreed well with the ionization

---

*Edwards (6) has given a detailed review of the studies on active nitrogen at very low temperatures.

potential, 14.545 e.v., calculated for the ^4S nitrogen atom (59). A second appearance potential was observed at 16.1 e.v., but not conclusively assigned. Another mass spectrometric study confirmed the appearance potential at 14.7 e.v., but did not detect the one at 16.1 e.v. (27).

The presence of N_3 in active nitrogen has been inferred from spectroscopic observations on both the gas phase (60) and on products condensed from active nitrogen at 4.2°K (61). However, infra-red absorption by Milligan *et al*. (61) in the solid phase was not confirmed (62), and the presence of N_3 remains controversial. It seems likely that N_3 should be rapidly destroyed by reaction with nitrogen atoms (63).

The majority of active nitrogen reactions can be explained on the assumption that nitrogen atoms, in the ^4S ground state, are responsible for its chemical reactivity. However, there are some reactions that suggest the possible presence of excited molecules as a second reactive species. Both vibrationally and electronically excited molecules have been suggested as this second species.

Vibrationally excited ground state molecules were first proposed by Evans and Winkler (63), as the second reactive species, and experimental evidence for their presence has been obtained by several workers. For example, Kaufman and Kelso (64) found that addition of either nitrous oxide, or carbon dioxide, downstream from the discharge removed vibrationally excited nitrogen molecules. They also observed that when nitric oxide was added to the point of extinction of the afterglow, followed by addition of nitrous oxide downstream, the effect was greater. The rate of decay of the excited molecules was of approximately the same order of magnitude as that of the decay of vibrationally excited oxygen molecules (65).

The presence of vibrationally excited ground state molecules in active nitrogen has been demonstrated directly from their vacuum ultraviolet absorption spectrum (66), and indirectly by studies of the thermal effects of active nitrogen when it is examined with an isothermal probe (67).

More recently, Starr (68) and Starr and Shaw (69) have demonstrated the transfer of vibrational energy from nitrogen molecules to electronic energy of sodium and potassium.

It seems reasonable, from the numerous studies on vibrationally excited molecules in active nitrogen, that the energetics of this species is sufficient for a limited extent of reactivity, e.g. decomposition of ozone (70). However, it seems unlikely that their presence can account for reactions that require more than about 25 Kcal for their initiation (70).

Of the possible excited molecular species in active nitrogen, that might be effective in chemical reactions, the $N_2(A^3\Sigma_u^+)$ species seems to be the only one with a life-time sufficient to permit its presence in appreciable concentrations, under the usual experimental conditions, for studying chemical reactions.

A lower limit of 10^{-2} sec. for the radiative life-time of the $N_2(A^3\Sigma_u^+)$ state was obtained by the molecular beam experiment of Lichten (78). Other values have been obtained by various methods, e.g. 0.026 sec., by absorption spectroscopy (79); about 1 sec., from the emission of the Vegard-Kaplan bands in the Lewis-Rayleigh afterglow, at pressures 20-760 mm Hg (80); 2.0 ± 0.9 sec., by combination of absorption and emission spectroscopy (81); 0.9 sec., by measuring the intensity of the (0,6) Vegard-Kaplan band (82); 0.08 ± 0.04 and 0.084 sec., from studies on the decomposition of ammonia by active nitrogen (52,72); and 1.1 sec., from studies of the reactions of iodine (83). A recent attempt by Young (84), to measure the actual life-time of $N_2(A^3\Sigma_u^+)$, gave only a very small upper limit $\approx 5 \times 10^{-4}$ sec.

Studies on the decomposition of ammonia, water and sulfur dioxide have been particularly suggestive of a second reactive species (71,72,138,141). The maximum extent to which ammonia may be decomposed was found to be about one-sixth the activity of the active nitrogen determined from its ability to form hydrogen cyanide from ethylene. Somewhat similar conclusions have been reached for the reactions with water and sulfur dioxide. It would appear, therefore, that these inorganic molecules react with a different species in the active nitrogen than does ethylene. Furthermore, mass spectrometric studies have shown that the decomposition of ammonia is not accompanied by decrease in the nitrogen atom concentration (73). It has been proposed, therefore, that the decomposition of ammonia is due to energy transfer from excited nitrogen molecules (72,73).

The reactions of active nitrogen with ethane, propane and neopentane, investigated by Winkler and co-workers (75,76), also suggested a second reactive species; it might well be $N_2(A^3\Sigma_u^+)$ in relatively low vibrational levels.

Freeman and Phillips (77) made a photometric study of the flame produced when iodine vapour was mixed with active nitrogen. Nitrogen atoms were consumed in the first region of the flame and nitrogen molecules in an excited, probably the $A^3\Sigma_u^+$, state were produced. They suggested this reaction as a means of producing $A^3\Sigma_u^+$ molecules, for studying their behaviour in the absence of nitrogen atoms.

DETERMINATION OF NITROGEN ATOM CONCENTRATION

In the reaction of active nitrogen with ethylene, the maximum hydrogen cyanide production ('plateau' value), in a cylindrical reaction vessel, has been found to be independent of ethylene flow rate and temperature, in the region 40° to 400°C (72,85). Closely similar plateau values were obtained from a variety of saturated and unsaturated hydrocarbons and their derivatives. Accordingly, it seemed reasonable to suggest that the nitrogen atom concentration in active nitrogen might be estimated from this maximum production of hydrogen cyanide from, say, ethylene. As a difficult alternative, it is necessary to explain an essentially equal loss of nitrogen atoms during the reactions of such dissimilar molecules as C_2H_4, C_3H_6, C_3H_8, C_4H_{10}, cyclo - C_5H_{10}, and CH_3Cl.

On the other hand, when nitric oxide is added to a stream of active nitrogen a very fast reaction occurs (74,86, 87,88), usually assumed to be:

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

This reaction has been used for the 'gas phase titration' of nitrogen atoms. With a flow rate of nitric oxide less than that of nitrogen atoms, consumption of nitric oxide, by reaction (1), leads to the formation of oxygen atoms, which can then react with the residual nitrogen atoms to form excited nitric oxide molecules. These emit a blue glow (β and γ bands of nitric oxide), according to the reaction,

$$N + O + M \rightarrow NO^* + M \rightarrow NO + h\nu \qquad (2)$$

The occurrence of reaction (2) was demonstrated by Kaufman and Kelso (88), who added $N^{15}O$ to a stream of active nitrogen from $N_2{}^{14}$, and found only $N^{14}O^*$ to be formed.

When sufficient nitric oxide is added to remove all the nitrogen atoms, the cessation of light emission corresponds to the equivalence or end-point of the 'titration'. With a slight excess of nitric oxide, hence consumption of all the nitrogen atoms, reaction of the excess nitric oxide with oxygen atoms produces excited NO_2^*, which emits a yellow-green continuum. In practice, the colour change, from blue to yellow-green emission, provides a relatively easy identification of the end-point for the 'titration'. This method for estimating the nitrogen atom concentration is fast and has been used extensively in recent years.

A lively controversy, of which only the main elements will be discussed here, has existed for some time on the relative merits of the hydrogen cyanide and nitric oxide methods for determining nitrogen atom concentrations. This resulted from an observation by Verbeke and Winkler (74) that the ratio 'maximum NO decomposed': 'maximum HCN formed from C_2H_4' (the NO/HCN ratio) appeared to vary from about 1.4 to 2.4, in the pressure range 1 to 16 mm Hg, a discrepancy which they suggested might be due to reaction of nitric oxide with both nitrogen atoms and a second species, presumably excited nitrogen molecules. This interpretation was criticized by Zinman (90), who claimed that the results could be explained in terms of nitrogen atoms only. However, his treatment, in turn, was criticized by Wright et al. (72), who found, contrary to the prediction of Zinman's equation, that the NO/HCN ratio did not depend on the number of carbon atoms in the hydrocarbon molecule. They also observed that it was independent of the mode of excitation of molecular nitrogen and of the nitrogen atom concentration. On the other hand, it changed with time of decay of the active nitrogen. A consideration of the NO/HCN, $NH_3{}^*$/HCN and NH_3/NO ratios, after different times of

---

[*] Where NH_3 here represents the maximum amount of ammonia decomposed under comparable conditions.

decay, led them to suggest that both the ammonia and nitric oxide reactions might involve electronically excited nitrogen molecules.

Back and Mui (89) found an almost stoichiometric relation between nitric oxide consumption and the formation of $N^{14}N^{15}$, when $N^{15}O$ reacted with nitrogen atoms produced in a stream of N_2^{14}. This suggests that the consumption of NO is a valid measure of the nitrogen atom concentration.

In contradiction to the conclusions of Back and Mui, Fersht and Back (91) subsequently obtained data that seemed to support the validity of the hydrogen cyanide yield from ethylene, as a measure of the nitrogen atom concentration. They reacted active nitrogen with various mixtures of ethylene and nitric oxide, at 1 mm pressure. The sum of hydrogen cyanide produced and nitric oxide consumed remained almost constant, and equal to the hydrogen cyanide yield from pure ethylene, until the mixture was about 50% in nitric oxide. It was concluded that nitric oxide can also react with excited molecules, probably in the $A^3\Sigma_u^+$ state.

A mass spectrometric study has been made of the reaction of active nitrogen with ethylene, when 2% of hydrogen was added to the nitrogen stream through a microwave discharge (93). The yield of hydrogen cyanide was then brought into closer correspondence with the estimates of nitrogen atom concentration based on the nitric oxide titration. Accordingly, a mechanism was proposed which sought to explain an inefficiency for production of hydrogen cyanide in the ethylene reaction, due to loss of nitrogen atoms in hydrogen abstraction reactions from free radicals, to yield NH radicals, followed by their reaction with nitrogen atoms, or by their disproportionation. However, it should be noted, perhaps, that the concentration of hydrogen atoms produced in the discharge was undoubtedly far greater than that normally present in active nitrogen reactions with hydrocarbons.

The chemical estimation of nitrogen atom concentrations has been recently compared with their physical estimation in an electron spin resonance spectrometer (E.S.R), calibrated against molecular oxygen (94). The results agreed well, in the pressure range 0.4 to 3 mm Hg, with those obtained with the nitric oxide titration. However, the comparison is apparently subject to possible complications, as shown by Weyssenhoff and Patapoff (95). They, too, used an E.S.R spectrometer, but made only relative measurements of the nitrogen atom concentration for different operating conditions, to avoid uncertainties due to calibration of the E.S.R unit. Although the nitric oxide titration and E.S.R values agreed in the range of 1.6 to 5.1 mm Hg, when the flow velocities were relatively slow, the nitric oxide values became much larger than those given by E.S.R (by as much as 1.37 to 1.66) for higher flow velocities at pressures above 3 mm Hg.

Vacuum-ultraviolet absorption measurements of the resonance lines of nitrogen atoms, by the line absorption method, also corroborate the validity of the gas phase nitric oxide titration technique (96).

A seemingly incontrovertible physical method for measuring the nitrogen atom concnetration was attempted unsuccessfully by Back and Winkler (155), and finally brought into successful operation by Elias (97). It involves measurement of the pressure decrease due to atom recombination, when a portion of the dissociated stream of active nitrogen is rapidly isolated in a section of the flow line. The results obtained were in excellent agreement with the values obtained by the nitric oxide titration.

It is interesting, perhaps, that Dubrim *et al*. (92) have produced ^{13}N atoms by nuclear techniques, and reacted them with various mixtures of ethylene and nitric oxide at 1 atm. and 25°C. They suggested that ground state, $N(^4S)$, atoms cannot react efficiently with ethylene to form hydrogen cyanide or any other product, but may react readily with nitric oxide. On the other hand, a second reactive species, probably an excited nitrogen atom, might be formed by their method, and be capable of reaction with ethylene as well as with nitric oxide.

Although the maximum hydrogen cyanide yield from ethylene cannot be dismissed summarily as a valid measure of nitrogen atom concentration [e.g. closely similar yields from a variety of hydrocarbons and their derivatives, the experiments of Fersht and Back (91)], nevertheless, the evidence in favour of the nitric oxide titration would seem to be overwhelming.

This is particularly true, perhaps, for the nitrogen atom recombination method discussed above, since it is difficult to conceive of any uncertainty in the interpretation of the measured pressure decrease.

CHEMICAL REACTIONS OF ACTIVE NITROGEN

A number of earlier studies, particularly those of Strutt, indicated that active nitrogen was very reactive chemically. Vapours of mercury, zinc, cadmium and arsenic were converted to nitrides; carbon disulphide, sulphur chloride and hydrogen sulphide yielded a polymeric nitrogen sulphide; hydrocarbons produced hydrogen cyanide accompanied by the emission of CN bands, from a lilac-colour reaction flame; nitric oxide reacted with active nitrogen very rapidly, and the only product was NO_2 (3). An early study of this reaction (98) laid the basis for the 'gas phase titration' of nitrogen atoms, mentioned previously, the suggested mechanism being:

$$N + NO \rightarrow N_2 + O$$

$$O + NO \rightarrow NO_2$$

Reaction of active nitrogen with atomic hydrogen was found to yield trace quantities of ammonia, whereas molecular hydrogen was not affected (99). Hydrogen bromide, hydrogen iodide and ammonia were found to be decomposed by active nitrogen, but no reaction was observed with oxygen or carbon monoxide (19).

A systematic study of the chemical reactions of active nitrogen was begun in 1949 at McGill University by Winkler and his associates. A number of kinetic investigations of the reactions of organic and inorganic compounds have now been made in this, and other laboratories. In practically all cases, the reactant was introduced as a gas into a stream of active nitrogen, produced by either condensed or microwave discharge, in a fast gas flow system. After reaction, the products were collected in downstream traps, cooled at very low temperatures, and analysed by appropriate methods.

Comments on these studies will be limited mainly to those reactions that have direct relevance to the present investigation, since reasonably comprehensive reviews are available for the interested reader (4,5,6,7).

REACTIONS WITH ORGANIC COMPOUNDS

The reaction of active nitrogen with ethylene, by Greenblatt and Winkler (101), was the first to be investigated kinetically in any detail. The main product was hydrogen cyanide, with small amounts of ethane, and a hydrogen cyanide polymer. They proposed the following mechanism:

$$C_2H_4 + N \rightarrow \begin{matrix}\text{Activated}\\ \text{Complex}\end{matrix} \rightarrow HCN + CH_3^{\bullet}$$

$$N + CH_3 \rightarrow HCN + 2H$$

The formation of ethane could be explained by hydrogenation of

C_2H_4 or by recombination of $CH_3^{\bullet}$ radicals.

Reinvestigation of the reaction (102) showed that cyanogen, acetylene and methane,were also formed in small amounts. Alternative to the simple mechanism proposed in the first study, it was suggested that other possible reactions were:

$$C_2H_4 + N \rightarrow \begin{matrix}\text{Activated}\\\text{Complex}\end{matrix} \rightarrow CH_2 + CH_2N$$

$$CH_2N \rightarrow HCN + H$$

$$CH_2 + N \rightarrow HCN + H \ .$$

The formation of cyanogen was explained as:

$$C_2H_4 + N \rightarrow [C_2H_4N]^*$$

$$[C_2H_4N]^* + N \rightarrow [C_2H_4N_2]^* \rightarrow C_2N_2 + 2H_2 \ .$$

Dehydrogenation of ethylene, by hydrogen atoms, might produce the small amounts of acetylene

$$C_2H_4 + H \rightarrow C_2H_3 + H_2$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \ ,$$

while methane might be formed by

$$CH_3 + H_2 \rightarrow CH_4 + H$$

$$CH_3 + H + M \rightarrow CH_4 + M \ .$$

Traces of ammonia have been detected in the products of the ethylene reaction (72,103). The ammonia formation can be explained by the combination of nitrogen and hydrogen atoms (104).

Other unsaturated hydrocarbons

A number of other unsaturated hydrocarbons have also been investigated. These are propylene (85,105,106), the butenes (107), acetylene and methylated acetylenes (108,109). In all cases, hydrogen cyanide was the main product isolated.

Alkanes

The reactions of active nitrogen with alkanes, such as methane (75,110,111,112), ethane (75,76,110,111), propane (75,76,113), the butanes (114), and neopentane (75,76,115), have been studied. The main feature of these reactions is that the alkanes react less rapidly than the corresponding alkenes, again, to produce hydrogen cyanide as the preponderant nitrogen containing product.

Cycloparaffins

The reactivities of cycloparaffins with active nitrogen were found to increase in the order cyclopropane, cyclobutane, cyclopentane (116), and hydrogen cyanide was the principal product from all three reactants. The reaction of cyclopropane has been found to be strongly inhibited in the presence of ammonia (85).

Other organic compounds

These include azomethane (117), alkyl chlorides (118), chloromethanes (161), methylamine (119), methyl cyanide (120), mercury diethyl (121), methanol (122), ethanol (123), and cyanogen (124). In all of these reactions too, with the exception of CCl_4, (which gave CNCl), and $(CN)_2$, which suffered decomposition, the main nitrogen containing product was hydrogen cyanide.

In 1956, Evans et al. (100) presented a review of the reactions of active nitrogen with various organic compounds, and proposed a 'unified' mechanism based on nitrogen atoms in the ^4S ground state as reactive species. They suggested that the initial reaction with ethylene was:

$$N + C_2H_4 \rightarrow N.C_2H_4 \rightarrow HCN + CH_3^{\cdot} + 62 \text{ Kcal.}$$

This reaction involves a change of spin from three unpaired electrons in the nitrogen atom to one in the methyl radical, and the transfer of a hydrogen atom from one carbon atom to another. A relatively long-lived complex might be formed by the nitrogen atom and the ethylene molecule to allow both the change of spin and the movement of the hydrogen atom to occur. The methyl radicals then react with nitrogen atoms very rapidly,

$$N + CH_3^{\cdot} \rightarrow HCN + 2H + 10 \text{ Kcal.}$$

This reaction is spin-allowed for three out of eight collisions and might be expected to have a small activation energy. The two hydrogen atoms can recombine to a hydrogen molecule, or react with the parent hydrocarbon, or other radicals, to yield stable products.

The assumption of a relatively long-lived reactant-nitrogen atom complex was the basis for the formulation of a 'unified' mechanism for reactions of active nitrogen with organic molecules. The main features can be illustrated by comparison of the proposed mechanisms for the propylene, propyl chlorides, and propane reactions:

$$N + C_3H_6 \rightarrow N.C_3H_6 \ ,$$

$$N + C_3H_7Cl \rightarrow N.C_3H_6 + HCl \ ,$$

$$N + C_3H_8 \rightarrow N.C_3H_6 + H_2 \ ,$$

with the formation of a chemically identical complex. Differences in the reactions were ascribed to the stability of the complex. Formation of unsaturated hydrocarbons, as secondary products, was explained mainly by nitrogen atom recombination involving the complex,

$$N + N.C_3H_6 \rightarrow C_3H_6^* + N_2 \rightarrow C_2H_4^* + CH_2 + N_2 \ .$$

By appropriate adaptation, the 'unified' mechanism may be applied to a variety of reactions of active nitrogen with organic compounds and their derivatives, and has provided a useful basis for discussing such reactions.

REACTIONS WITH ELEMENTS AND INORGANIC COMPOUNDS

Metals

Strutt (3) made a preliminary investigation of the reactions of active nitrogen with vapours of mercury, zinc, cadmium, sodium and arsenic. The products were exclusively nitrides.

A study of the reaction of active nitrogen with germane gave, as products, hydrogen and germanous nitride, whereas the corresponding reaction with boron trichloride yielded chlorine and tetrachlordiborine (156).

Brennen and Kistiakowsky (139) found that metal carbonyls react very rapidly with active nitrogen, to form metal atoms by a stepwise degradation.

The Nitrogen family

Perhaps the first reaction in this category that might be mentioned is the recombination of nitrogen atoms, either in the gas phase or on the walls of the reaction vessel,

$$N + N + M \xrightarrow{k_1} N_2 + M$$

$$N + W \xrightarrow{k_2} 1/2\ N_2 + W\ .$$

These reactions have been studied kinetically several times. The recombination reaction is predominantly homogeneous, and third order, at pressures above 2.5 mm Hg (127,129). Some of the rate constants for the homogeneous recombination, k_1, are: 1.0×10^{16} cc^2 $mole^{-2}$ sec^{-1} (125), 6.19×10^{15} (126),

5.7×10^{15} (127), 1.2×10^{16} (128), and 1.04×10^{16} (129). Below 2.5 mm Hg a pseudo-first order wall recombination becomes important, with a recombination coefficient $\gamma = k_2\, D/\overline{C}$ (where D = reactor diameter, and $\overline{C}$ = root mean square atomic velocity). Values of γ reported, for pyrex glass, are: $\gamma = 1.6 \times 10^{-5}$ (127), 3×10^{-5} (128), and 7.5×10^{-5} (129).

The reactions of active nitrogen with nitric oxide and ammonia have already been presented in preceding sections, and need not be further discussed.

The reaction with nitrogen dioxide has been studied by many investigators (73,74,86,130,131). The mechanism of the reaction appears to be:

$$N + NO_2 \rightarrow N_2O + O$$

$$N + NO_2 \rightarrow 2\ NO$$

$$N + NO_2 \rightarrow N_2 + O_2$$

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

$$N + NO \rightarrow N_2 + O$$

$$O + NO_2 \rightarrow NO + O_2$$

Rate constants of about 0.8×10^{-11} cm^3 molecule^{-1} sec^{-1} at 500^{o}K (74), and of 1.85×10^{-11} at 300^{o}K (131), have been reported.

Nitrous oxide has been found to deactivate vibrationally excited nitrogen molecules (64), and to undergo a very small decomposition, less than 5% at 300°C, with active nitrogen (74).

Khanna and Winkler (136) found that active nitrogen from a condensed discharge reacts very rapidly with white phosphorus vapours, to yield a mixture of nitrides. The extent of the reaction agreed with that given by the nitric oxide titration, in a system 'poisoned' with water vapour. However, in the 'unpoisoned' system the data did not agree with the value of the nitrogen atom concentration inferred from either the nitric oxide or the ethylene reaction.

Hydrogen and a reddish-brown polymer, $(PN)_n$, were the products of the active nitrogen-phosphine reaction (137). This reaction appeared to involve hydrogen abstraction by the nitrogen atoms.

Hydrogen, Halogens and Hydrogen halides

The reaction of active nitrogen with hydrogen atoms appeared to produce only small amounts of ammonia, and to result only in recombination of nitrogen atoms. No reaction was observed with molecular hydrogen, even at 350°C (104).

The reaction of iodine with active nitrogen has been discussed in a previous section, 'Reactive species in active nitrogen'. In the reaction with bromine, the spectrum of NBr was excited by the active nitrogen (133).

Wiles and Winkler (134) found hydrogen chloride to be decomposed by active nitrogen from a condensed discharge, with the production of chlorine. The extent of the reaction was limited, owing presumably to back reactions. On the other hand, the reaction of hydrogen bromide with production of bromine, and ammonia, occurred extensively (135).

The Oxygen family

Bett and Winkler (143) studied the reaction of active nitrogen with sulfur. The infrared spectra of the products showed that N_4S_4 and at least two other sulfur nitrides were present. They postulated two mechanisms, one based on the nitric oxide value, the other on the hydrogen cyanide value, for the nitrogen atom concentration.

Jacob et al. (141) investigated the reaction of active nitrogen with sulfur dioxide. The amount of SO_2 decomposed, by active nitrogen from a condensed discharge, in a system 'poisoned' with water vapour, increased with SO_2 flow rate to a limiting value that was about one-sixth the NO 'titration' value for the active nitrogen concentration. It appeared that SO_2 was decomposed by energy transfer from excited N_2 molecules. In agreement with Smith and Jolly (142), they observed no SO_2 decomposition by active nitrogen from a microwave discharge.

With hydrogen sulphide and carbon disulphide, a great deal of polymer was formed. Small amounts of ammonia were also formed in the hydrogen sulphide reaction (140).

Vadlamudy and Winkler (138) have recently studied the reaction of water vapour with active nitrogen from a condensed discharge. The maximum water decomposition represented about one-fifth of the nitrogen atom concentration, estimated from the nitric oxide 'titration'. The products were mainly hydrogen and oxygen, with traces of ammonia, nitrite and nitrate in solution in excess water present. A rate constant of 0.9×10^9 cc mole^{-1} sec^{-1} was estimated. They suggest that excited nitrogen molecules are the species responsible for the decomposition of water. Similar experiments with a microwave discharge gave no evidence of decomposition.

For the reaction of active nitrogen with oxygen atoms, in the absence of oxygen molecules, a rate constant of 1.83×10^{15} cc^2 mole^{-2} sec^{-1} has been obtained (129).

With molecular oxygen, Varney (144) observed small yields of N_2O, NO and NO_2. Kistiakowsky and Volpi (86) investigated the reaction of active nitrogen with oxygen by using the principle of a 'stirred reactor' and a mass spectrometer. Oxygen was found to react at elevated temperatures, but no reaction was observed at room temperature. Absence of any oxides of nitrogen among the reaction products, and the appearance of the β-bands of NO, suggested the following mechanism:

$$N + O_2 \xrightarrow{k_1} NO + O$$

$$N + NO \rightarrow N_2 + O \; .$$

They reported a rate constant for the first reaction,

$$k_1 = 2 \times 10^{12} \exp(-6{,}200/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

From studies on the effect of oxygen on the decomposition of NO in flames, $O + NO \rightleftharpoons O_2 + N$ and $N + NO \rightleftharpoons N_2 + O$, Kaufman and Decker (145) found, indirectly, $k_1 = 1.7 \times 10^{13} \exp(-7{,}500/RT)$ cc mole^{-1} sec^{-1}.

Mavroyannis and Winkler (146) have studied the maximum extent, the products, and kinetic characteristics of the oxygen reaction. The maximum production of oxygen atoms was found to correspond to the maximum amount of hydrogen cyanide produced under the same conditions. They detected small amounts of nitrous oxide, nitric oxide, and nitrogen dioxide in the condensable products. A rate constant $k_1 = 2.3 \times 10^{12} \exp(-5{,}900/RT)$ cc mole^{-1} sec^{-1} was calculated.

Clyne and Thrush (87) have also investigated the kinetics of the active nitrogen-oxygen reaction. They compared the yields of oxygen atoms produced when nitric oxide and oxygen reacted completely with active nitrogen. The mean value of $(O)_{NO}/(O)_{O_2}$, as determined by the nitrogen dioxide titration, was 1.02 ± 0.03, i.e. active nitrogen reacted to the same extent with oxygen and nitric oxide. The rate constant for the oxygen reaction was found to be:

$$k_1 = 8.3 \times 10^{12} \exp(-7{,}100/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

The conclusions of Mavroyannis and Winkler, relative to the extent of the oxygen reaction, are compatible with those of Clyne and Thrush only if the ratio NO/HCN were equal to unity in the two studies. However, without recording a numerical value for it, Mavroyannis and Winkler do state that the NO/HCN ratio was greater than unity in their study, and it must be concluded that a major discrepancy appears to exist between the two investigations.

ADDITIVES IN ACTIVE NITROGEN

In the course of the present investigation, some studies were made on the effect of certain additives to the nitrogen that was passed through the discharge tube. A few comments about some of the earlier analogous studies might therefore be appropriate.

Many years ago Rayleigh (3) observed that the 'Lewis-Rayleigh' afterglow was considerably brightened when certain gases were added to the discharged nitrogen. In some cases, this brightening occurred if the gas were added either before or after the discharge. Rather qualitative experiments were made with various compounds, which were then listed in decreasing order of effectiveness: H_2S, H_2O, CO_2, CO, C_2H_2, C_2H_6, CH_4, O_2, Hg, Cl_2, H_2, Ar, He, N_2. Experiments by Willey (147) established the efficiencies of CO_2, N_2O, N_2 and CO in the order mentioned.

Willey (148) studied the rate of decay of the afterglow in the presence of different gases. He found that, as the concentration of the impurity increased, the wall reaction diminished and the homogeneous decay increased, up to a limit of 0.1% of impurity present. Higher concentrations reacted chemically with the active nitrogen, and interfered with the normal decay.

Lewis (13) made experiments to ascertain whether the introduction of water vapour could restore the afterglow in pure nitrogen. He observed that the existence of the afterglow depended upon the presence of water vapour. Kaplan (149) was able to obtain the afterglow only by removing the slightest trace of hydrogen.

Rayleigh (150) made a careful experiment to study how the intensity of the afterglow varied when oxygen, in measured amounts, was mixed with nitrogen before the discharge. He concluded that the presence of oxygen gave rise to a layer on the glass that had a favourable effect on the afterglow.

Young et al. (151) have given some results on the effect of adding O_2, NO or SF_6, either before or after the discharge. Nitric oxide and oxygen were capable of increasing the number of atoms from the discharge to the same extent as SF_6, but much larger amounts had to be added.

The interaction of NO, O_2, NH_3, NF_3 and SF_6 with purified active nitrogen has been studied with a mass spectrometer (152). Addition before the discharge resulted in a threefold increase in the partial pressure of nitrogen atoms, whereas, with the exception of SF_6, addition after the discharge caused a twofold increase.

Anderson and co-workers (15,153,154) have studied the effect of O_2 and H_2, in different proportions, on the intensity of the nitrogen afterglow. They observed that, with pure nitrogen, the walls of the reaction vessel had a great affinity for hydrogen but practically none for oxygen.

THE PRESENT PROBLEM

As indicated previously, earlier studies by Mavroyannis and Winkler, and by Clyne and Thrush appear to be at variance in respect of the reactivity of active nitrogen towards molecular oxygen. The former found the maximum production of oxygen atoms to correspond to the maximum production of hydrogen cyanide from the ethylene reaction. On the other hand, the latter observed the maximum extent of the oxygen reaction to correspond to the maximum destruction of nitric oxide. Since Mavroyannis and Winkler found a NO/HCN ratio greater than unity (although the actual value was not reported), it must be concluded that there is a real discrepancy between the conclusions reached in the two studies.

The experimental conditions for the two studies were by no means identical. In particular, the analytical methods used to follow the course of the reaction were not the same. Apart from the different methods for estimating the nitrogen atom concentrations, the production of oxygen atoms was also determined in different ways. Mavroyannis and Winkler added excess nitrogen dioxide to the gas stream, with subsequent trapping and determination of the amounts of N_2O_3, while Clyne and Thrush 'titrated' the oxygen atoms with nitrogen dioxide in the gas phase.

The objective of the present work was to re-investigate the maximum extent of the reaction of active nitrogen with molecular oxygen, using both experimental techniques in a single system, with a view to obtaining, if possible, an explanation for the apparent discrepancy. In addition to the maximum extent of the reaction, values of its rate constant were obtained, as another criterion for comparison.

During the course of the investigation, some attention was given also to possible factors that might influence the NO/HCN ratio, on the assumption that there might be some conditions under which this ratio would become unity. If these conditions did exist, and might be ascribed to the system used by Clyne and Thrush, their yields of oxygen atoms might have corresponded to maximum yields of hydrogen cyanide from ethylene, had they made such experiments, and no real discrepancy with the other study existed. As part of this phase of the study, the effects, on the nitric oxide values, of certain additives, such as water, hydrogen and oxygen were examined.

As an incidental to the main study, a rough estimate of the rate constant for the reaction of nitric oxide with nitrogen dioxide was also obtained. No such value has been reported previously in the literature.

EXPERIMENTAL

MATERIALS

Bone dry, 99.7% pure, and dry, 99.995% pure, nitrogen were obtained from Linde Air Products Ltd. Any oxygen and water present were removed by passing the gas over copper turnings at 400° to 425°C, and through a liquid air trap.

Oxygen, of 99.5% purity (Liquid Carbonic Canadian Corp. Ltd.) was passed through a liquid air trap to eliminate traces of water.

Pre-purified hydrogen, 99.9% pure, was obtained from Matheson Co. Inc.

Nitric oxide, 99% pure, was obtained from Matheson Co. Inc., and further purified by trap-to-trap distillation through a column of 'caroxite', which is capable of absorbing nitrogen dioxide. The whole procedure was repeated many times, until all the nitrogen dioxide was removed, as indicated by the absence of blue N_2O_3 when the gas was passed into a trap cooled in liquid air.

Nitrogen dioxide was prepared by oxidation of pure nitric oxide with an excess of pure oxygen. When the reaction was complete, and the blue N_2O_3 was no longer visible in the condensed material, the excess oxygen was pumped off. The nitrogen dioxide was kept frozen, when not in use, to prevent its photochemical decomposition, and KEL-F stopcock grease was used in all parts of the apparatus in contact with the nitrogen dioxide. During the experiments, nitrogen dioxide was never allowed to come into contact with mercury, since it reacts instantaneously. Frequent checks were made for the presence of N_2O_3 and, whenever necessary, the oxidation was repeated.

Ethylene, 99.75% pure, was obtained from Matheson Co. Inc. It was frozen in a liquid air trap and any traces of air and non-condensable gases were pumped off. Further purification was made by two trap-to-trap distillations, in which only the middle fraction was retained.

APPARATUS

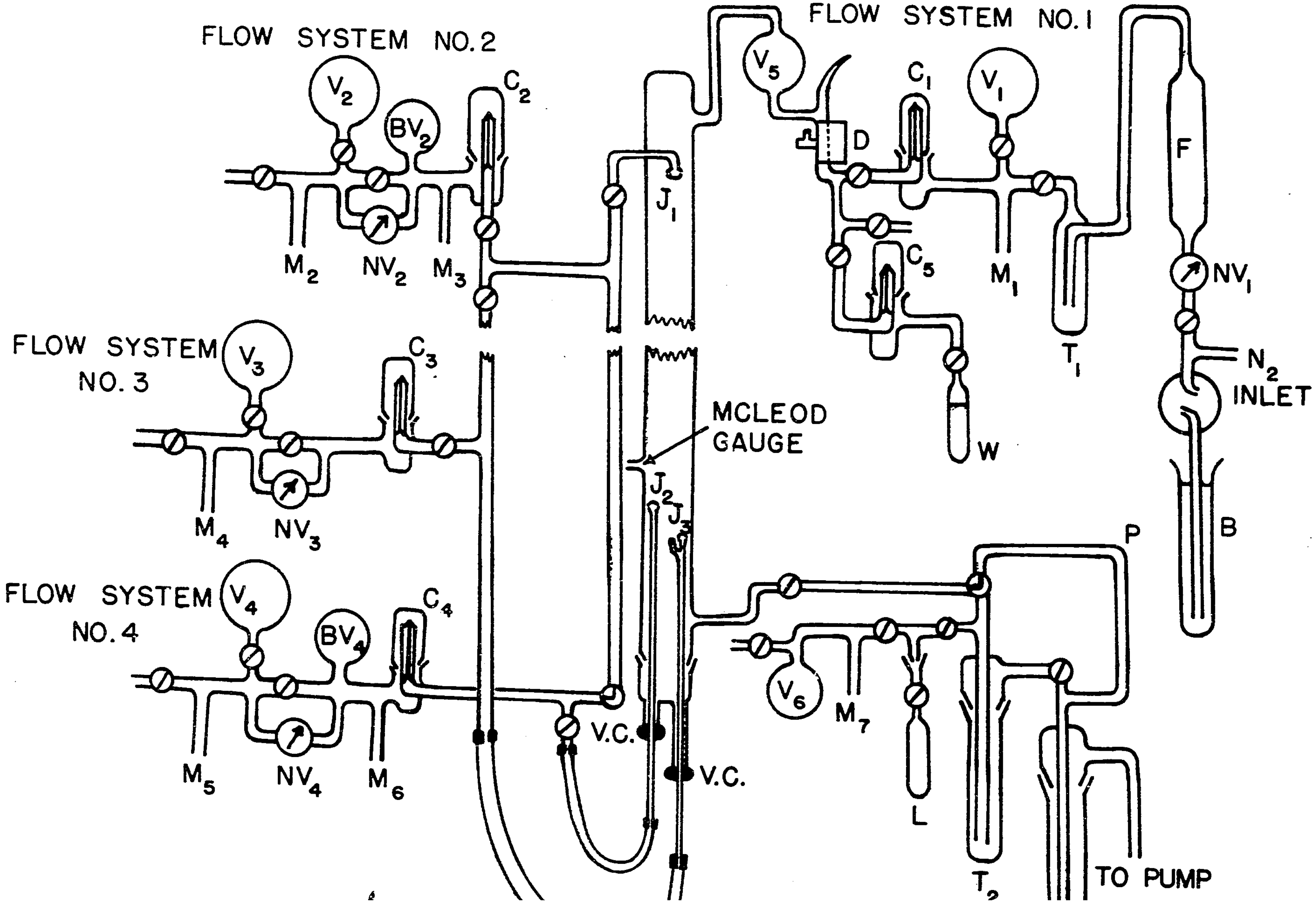
The apparatus employed was a fast flow vacuum system constructed entirely from Pyrex glass, except for the microwave discharge tube which was of quartz. The assembly is shown diagramatically in Fig. 3.

Nitrogen from a cylinder was passed through a manostat, B, containing di-butyl phthalate. The nitrogen then passed through a needle valve, NV_1, into a furnace, F, containing copper turnings at 400^o - 425^oC, to remove traces of oxygen. A liquid air trap, T_1, removed possible traces of water, after which the purified nitrogen was passed through a capillary flowmeter, C_1, into the discharge tube.

The discharge tube, made of quartz tubing 18 cm long and 12 mm I.D., was connected to the pyrex system by graded seals. The discharge was produced by a microwave unit, through the rectangular wave-guide, D.

Figure 3

DIAGRAM OF THE APPARATUS


FLOW SYSTEM NO. 2
V2
BV2
C2
M2
NV2
M3
J1
V5
FLOW SYSTEM NO. 1
C1
V1
D
F
C5
M1
NV1
T1
N2
INLET
W
B
FLOW SYSTEM NO. 3
V3
C3
M4
NV3
MCLEOD GAUGE
J2
J3
P
FLOW SYSTEM NO. 4
V4
BV4
C4
M5
NV4
M6
V.C.
V.C.
V6
M7
L
T2
TO PUMP

The discharged nitrogen was passed through a 300 c.c. bulb, V_5, prior to its admission to the reaction vessel. This allowed the 'pink' (Broida) glow to dissipate, and only the yellow Lewis-Rayleigh glow to be present in the reaction vessel proper.

The reaction vessel was a straight Pyrex tube, 80 cm long and 28 mm I.D. A fixed jet, J_1, was placed in the centre of the gas stream, about 8 cm below the inlet from the discharge. The jet was a bulb with five fine holes spaced at equal intervals around its circumference. At the bottom end of the reaction vessel were two vacuum couplings, V.C., (Veeco quick-vacuum couplings, type C). These were cemented, with epoxy resin, to tubes attached to the B40 ground joint. The two jets, J_2, J_3, with their lower ends connected by tygon tubing to the flow systems, could be moved through the couplings to any desired positions in the reaction vessel. These jets were also bulbs with four fine holes located symmetrically around their periphery.

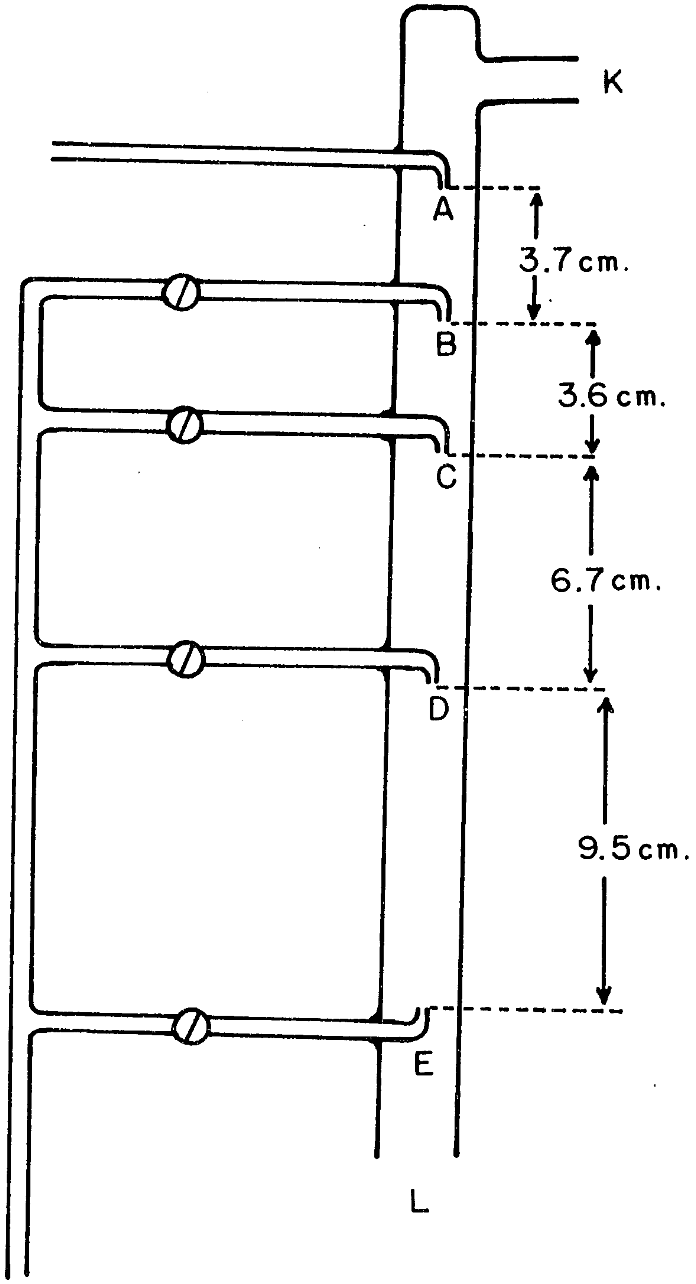
To obtain different reaction temperatures, the reaction vessel was heated with a suitable furnace that covered the entire length of the reactor. A narrow slit along the front of the furnace gave visibility for gas phase 'titrations' with either nitric oxide or nitrogen dioxide. The temperature inside the reaction vessel was measured with a copper-constantan thermocouple, placed in a well about 1 cm below the jet, J_3.

A second reaction vessel, Fig. 4, identical with the

<u>Figure 4</u>

SECOND REACTION VESSEL

(After Mavroyannis and Winkler, Ref. 146)


K
A
3.7 cm.
B
3.6 cm.
C
6.7 cm.
D
9.5 cm.
E
L

one constructed by Mavroyannis and Winkler (146), was used for some experiments. It consisted of a Pyrex tube 26 cm long and 22 mm I.D., with five small inlets at different points, as shown in Fig. 4.

Condensable gases that issued from the reaction tube were trapped in, T_2, at liquid air temperature. This trap could be easily isolated from the system, to permit distillation of the reaction products into a small detachable trap, L. A second liquid air trap, T_3, protected the pump from harmful gases. Another pumping route, P, permitted the trap, T_2, to be by-passed through a three-way stopcock.

Three flow systems, which may be designated as No. 2, No. 3 and No. 4, were connected to the reaction system. Flow system No. 2 could be connected to either jet, J_1, or jet, J_3. Flow system No. 3 was connected to the same jets, but used almost exclusively for jet, J_3. Flow system No. 4 was connected to jet, J_2, as well as to jets, J_1 and J_3. It was used primarily for jet, J_2, and occasionally for jet, J_1.

The flow systems, No. 2 and No. 4, each consisted of a large known volume, (V_2, V_4), a smaller ballast volume, (BV_2, BV_4), a capillary flowmeter, (C_2, C_4), a needle valve, (NV_2, NV_4), and two manometers (M_2M_3 and M_5,M_6). Flow system No. 3 was essentially the same, but without a ballast volume and second manometer.

Controlled, small amounts of water vapour, hydrogen or oxygen were added to the nitrogen, for some experiments. The water vapour system consisted of a reservoir, W, and a capillary flowmeter, C_5. Since the vapour pressure of the water remained essentially constant, at room temperature, a constant amount of water, approximately 0.1 x 10^{-6} moles/sec, passed through the capillary into the nitrogen stream. About the same amount of hydrogen or oxygen could be admitted to the system by another line.

The main pump was a Hypervac 23, which gave an ultimate vacuum of at least 5 x 10^{-3} mm Hg. A Duo-Seal vacuum pump was used for purification of reactants, evacuation of absorbers, etc. Pressures were measured with a McLeod gauge.

THE MICROWAVE DISCHARGE

Active nitrogen was produced in a high frequency microwave discharge, generated with a microwave diathermy unit manufactured by Raytheon Manufacturing Co. ('Microtherm', No. KV-104F, Model CMD-13). The maximum rated output was 125 watts, at a frequency of 2450 Mc/sec. The input voltage was supplied from a Sola constant voltage transformer. After a warm-up period of three minutes, the discharge was initiated with a Tesla coil, and the power subsequently held constant at 90% of the maximum value.

The microwave discharge has the advantage, over a condensed discharge between electrodes, of producing a more constant active nitrogen concentration for longer periods of time.

MEASUREMENT OF FLOW RATES

(a) Nitrogen

Nitrogen was allowed to flow through the apparatus. The needle valve, NV_1, was adjusted until the desired pressure in the reaction vessel was indicated by the McLeod gauge. At the same time a constant pressure head was obtained on manometer, M_1. The nitrogen flow rate was determined from the rate of evacuation of a known volume, V_1, for different pressure differentials across the flowmeter, C_1, measured on manometer, M_1.

(b) Oxygen, Ethylene, Nitric oxide

The known volume of the flow system, and the ballast volume, contained one of these reactant gases at the beginning of each experiment. The pressure of the gas in the known volume was kept much higher than the pressure in the ballast volume. After the reaction was begun, the pressure (flow head) in the ballast volume was kept constant by manipulating the needle valve. The average flow rate of the gas during the experiment could be accurately determined by measuring the pressure difference in the known volume before and after the experiment, assuming applicability of the ideal gas law, i.e.

$$\frac{dP}{dt} = \frac{dn}{dt}\frac{RT}{V} \quad \text{or} \quad \frac{dn}{dt} = \frac{dP}{dt}\frac{V}{RT}$$

where $\frac{dn}{dt}$ is the molar flow rate, $\frac{dP}{dt} = \frac{\Delta P}{dt}$, V = calibrated volume, R = gas constant and T = ambient temperature.

(c) Nitrogen dioxide

Flow rates of nitrogen dioxide were controlled by a stainless-steel needle valve, and measured by a capillary flowmeter. The flow rate was determined as described above for the other reactant gases. However, N_2O_4 was present initially in the known volume in equilibrium with NO_2, and, in the experiments, it dissociated completely when it entered the reaction vessel at the lower pressure of a few mm Hg.* Hence, a correction factor had to be applied to $\frac{dP}{dt}$ in calculating the flow rate of NO_2 into the reaction vessel. In computing the correction factor, both the fraction of N_2O_4 present in the gas, in the known volume, and the change of the dissociation constant with pressure, were considered. The values for the dissociation constant of the

$$N_2O_4 \rightleftharpoons 2NO_2$$

equilibrium were taken from Verhoek and Daniels (157). The pressure of the nitrogen dioxide was measured by manometers containing di-butyl phthalate (density at 25°C, 1.045 gr/cm^3).

EXPERIMENTAL PROCEDURE

The system was kept under vacuum except when it was

---

*The complete dissociation of N_2O_4 is not valid at higher pressures in the reaction vessel. In that case the degree of dissociation of N_2O_4 should be taken into account, in calculating the flow rate of NO_2.

necessary to re-grease the stopcocks. All stopcocks and ground joints, except those in contact with nitrogen dioxide, were greased with Dow-Corning high-vacuum silicone grease.

For high temperature experiments, the furnace of the reaction vessel was turned on, and the experiment started when the desired temperature was achieved, as measured by the thermocouple. Before each experiment the traps, T_1, T_2 and T_3, were immersed in liquid air, and the system was checked for leaks with the McLeod gauge. The nitrogen flow was then started, the microwave discharge put into operation, and allowed to operate for about one hour to obtain a constant concentration of active nitrogen. The pressure in the reaction vessel was measured before starting the reaction, whereas the temperature was recorded during the experiment. Reaction was initiated by turning on the flow of oxygen, which was maintained at the desired value by manipulating the needle valve, NV_2, to keep the flow head of the manometer, M_3, constant (Fig. 3).

The production of oxygen atoms was followed by either the nitrogen dioxide gas-phase 'titration', or by condensation of N_2O_3 in the presence of excess nitrogen dioxide. In the former method, nitrogen dioxide was admitted to the reaction vessel, at a point 5 cm below the oxygen inlet, and its flow rate increased until a yellow-green glow gave way to a dark end-point. In the latter method, considerable excess of nitrogen dioxide was added, also 5 cm below the oxygen inlet, and the resultant N_2O_3 subsequently condensed into trap, T_2.

The reaction was stopped, by using the by-pass, P, after a desired time interval, measured accurately with a stopwatch. At the same time, the flows of nitrogen dioxide and oxygen were shut off, while that of active nitrogen was maintained through trap, T_3, for subsequent experiments. The trap, T_2, containing N_2O_3 and non-condensables, was thus isolated from the system and evacuated, to 5 microns, with the auxiliary pump. The liquid air surrounding this trap was then removed, and the N_2O_3 allowed to distil into the trap, L, of the analytical system.

For measurements of rate constants, oxygen (flow system No. 2) was introduced into the reaction vessel through the top fixed jet, J_1. Nitric oxide (flow system No. 4) was admitted to the reaction vessel through the movable jet, J_2, located 50 cm below the top fixed jet, J_1. Introduction of nitric oxide not only stopped the reaction, by removing all the nitrogen atoms, but also provided a measure of the nitrogen atom concentration at that point. An excess of nitrogen dioxide (flow system No. 3) was then admitted to the reactor through the second movable jet, J_3, located 5 cm below the first movable jet, J_2, and the resultant N_2O_3 condensed as described above.

During the present investigation a coil of silver wire was placed prior to the trap, T_2, to facilitate oxygen atom recombination, and thus prevent ozone formation in the trap (146).

MEASUREMENT OF N- AND O-ATOM CONCENTRATIONS

The present investigation required measurements of nitrogen and oxygen atom concentrations. As indicated previously, nitrogen atom concentrations were measured by using either the nitric oxide gas-phase 'titration', or the maximum hydrogen cyanide production from ethylene. On the other hand, oxygen atom concentrations were determined by either the nitrogen dioxide gas-phase 'titration' or the method based on addition of excess nitrogen dioxide.

The nitric oxide gas 'titration', for nitrogen atoms, has already been discussed ('Determination of nitrogen atom concentration', P. 18), and need not be elaborated further.

When the hydrogen cyanide method was used for determining nitrogen atom concentrations, hydrogen cyanide was initially collected in trap, T_2, which, in turn, was evacuated to 5 microns to remove non-condensables. The liquid air surrounding the trap, T_2, was then removed, and a thick layer of carbon tetrachloride was frozen on the trap by immersing it, several times, in carbon tetrachloride. As the carbon tetrachloride later melted, the hydrogen cyanide distilled slowly, with almost no polymerization, into the detachable trap, L, which contained about 15 cc of distilled water, previously evacuated and frozen in liquid air. After the distillation was complete, the trap was removed and warmed to room temperature. The solution was then made alkaline with 5 ml ammonium hydroxide solution (5 N) and titrated with silver nitrate, using 2 ml potassium iodide 10% as indicator (158).

To determine the oxygen atom concentration by a gas-phase 'titration', nitrogen dioxide was added to the reaction mixture, to promote the simple and very fast reaction (98,159),

$$O + NO_2 \rightarrow NO + O_2 \quad .$$

With a flow rate of nitrogen dioxide less than that of oxygen atoms, all the nitrogen dioxide was consumed to form an equivalent amount of nitric oxide. The resultant nitric oxide could then react with the residual oxygen atoms to produce excited nitrogen dioxide, which emitted a yellow-green continuum. However, when an amount of nitrogen dioxide equivalent to the O-atom flow rate was added, the glow was completely and sharply extinguished, and this flow rate of NO_2 was taken to correspond to the O-atom concentration.

The other method, used by Mavroyannis and Winkler (146) to measure oxygen atom concentrations, involved addition of excess nitrogen dioxide, such that the oxygen atoms reacted rapidly to form a corresponding amount of nitric oxide. The resultant nitric oxide, in the presence of excess nitrogen dioxide, yielded N_2O_3, which was finally condensed, as described earlier, into the evacuated trap, L, immersed in liquid air to a fixed mark.

A known pressure of oxygen, measured by the manometer, M_7 (with concentrated sulfuric acid, density 1.84 gr/cm^3, as manometric fluid), was admitted from a storage bulb, after which the stopcock of the trap, L, was shut off and the liquid air removed to permit oxidation of the N_2O_3,

$$2N_2O_3 + O_2 \rightarrow 4NO_2 \ .$$

After several minutes, when the oxidation was complete, the trap was again immersed in liquid air, and the pressure measured. The difference between the two readings gave the pressure of oxygen consumed at liquid air temperature.

The amount of oxygen consumed was calculated from the relation:

$$O_2 = \frac{\Delta P}{R} \left(\frac{V'}{T'} + \frac{V_L}{T_L}\right)$$

where $\Delta P = P_1 - P_2$

R = Gas constant

V' = Volume of V_6 plus tubing

T' = Ambient temperature

V_L = Volume of trap, L

T_L = Liquid air temperature.

Since a temperature gradient existed between V' and V_L, this relation was not completely accurate (160). To reduce the error, the temperature, T_L, was replaced by an 'effective temperature' obtained by measuring the pressure exerted by a known amount of nitrogen under the same conditions. The 'effective temperature' was found to be about 81^oK.

The amount of nitric oxide, hence the oxygen atom concentration, was found by multiplying by two the amount of oxygen consumed, since from the oxidation reaction one mole of oxygen is equivalent to two moles of N_2O_3 (or NO). Although this method was time consuming, it was preferred, since it eliminated the difficulty of accurately determining flow rates of nitrogen dioxide.

'Blank' experiments, with known amounts of nitric oxide, were made to establish the validity of this method. The conditions were the same as those that prevailed later in the reaction of active nitrogen with oxygen, except that nitrogen flowed through the apparatus without the microwave discharge. Nitric oxide, at a known flow rate, was introduced into the reaction tube through the jet, J_2, located 60 cm below the top fixed jet, J_1. An excess of nitrogen dioxide was admitted to the system through the jet, J_3, 5 cm below the point at which nitric oxide was introduced, i.e., 5 cm below jet, J_2. The resultant N_2O_3 was subsequently trapped and determined as described previously.

All experiments were made at either room temperature, or at about 400°C, at a pressure of 2 mm Hg. This method was about 97% efficient for estimating nitric oxide concentrations, as shown in Table 1. A correction factor of 1.03 was therefore used when the method was applied in the subsequent experiments with oxygen.

Table 1

'BLANK' EXPERIMENTS FOR THE TRAPPING OF NITRIC OXIDE, BY USING EXCESS NITROGEN DIOXIDE*

Known NO moles/sec x 10^6	Trapped NO moles/sec x 10^6	Efficiency %
1.57	1.53	97.5
1.75	1.72	98.3
1.79	1.70	95.0
2.09	2.03	97.1
3.10	3.00	96.8

Average efficiency: 97%

---

*It should be emphasized, for reasons that will appear later, that this check of the analytical method, was made with the long-tube reactor, and not with the Mavroyannis-Winkler type of reactor.

RESULTS

THE REACTION WITH OXYGEN

Comparison of N- and O-atom concentrations, estimated by different methods

No quenching of the familiar yellow afterglow was observed when oxygen was introduced into the stream of active nitrogen, at room temperature. At higher temperatures, above about 100°C, and with increasing oxygen flow rates, the yellow glow gave way to a blue glow. The blue glow was observed at lower oxygen flow rates, as the temperature was increased, while, at a given temperature, increase of oxygen flow rate caused a gradual colour change from yellow (afterglow) to blue, to darkness, to pale yellow-green. The blue glow was due to the β and γ bands of nitric oxide, whereas the yellow-green glow represented the air-glow continuum, emitted by excited nitrogen dioxide. The yellow-green glow has been reported in only one earlier study (87), whereas the other observations have been made on at least three previous occasions (86,87,146).

In the present investigation, the extent of the active nitrogen-oxygen reaction was first examined by using the nitric oxide and nitrogen dioxide 'titration' techniques, for measuring nitrogen and oxygen atom concentrations respectively.

The active nitrogen concentration, at a certain definite level in the reactor, was determined by 'titration' with nitric oxide to the end point. After the end point was established, the corresponding nitric oxide flow rate was maintained steady, while nitrogen dioxide was admitted 5 cm below the nitric oxide jet, to 'titrate' the oxygen atoms that resulted from the N + NO reaction.

Similar experiments were made, in turn, with molecular oxygen. Oxygen was introduced into the stream of active nitrogen, at the same point that nitric oxide had been admitted previously. The production of oxygen atoms in the $N + O_2$ reaction was then estimated by the nitrogen dioxide 'titration', by adding nitrogen dioxide 5 cm below the inlet point of oxygen. Increasing flow rates of oxygen were used, until the maximum oxygen atom production was attained.

In Table 2 are recorded the yields of oxygen atoms produced when nitric oxide and oxygen, respectively, reacted completely with active nitrogen, at 2 mm Hg pressure, at different temperatures and at different levels in the reaction tube.

In a second series of experiments, nitrogen atom concentrations were estimated by the maximum hydrogen cyanide production from ethylene, and oxygen atom concentrations, from the active nitrogen-oxygen reaction, by the method based on addition of excess nitrogen dioxide, to form N_2O_3.

Hydrogen cyanide production was determined 60 cm below the fixed jet, all experiments being made at 400°C, and at pressures of 1 and 2 mm Hg. The results are shown in Table 3, and Figs. 5 and 6. Maximum oxygen atom concentrations were then determined, for the same conditions as those that prevailed during the corresponding reaction with ethylene. Oxygen was also admitted to the stream of active nitrogen, at a point 60 cm below the fixed jet, and excess nitrogen dioxide added 5 cm below this point, to form N_2O_3, which was trapped and estimated as outlined previously. The maximum oxygen atom concentrations thus determined, at 400 ± 2°C, and at pressures of 1 and 2 mm Hg, are shown in Table 4.

RATE CONSTANTS FOR THE $N + O_2$ REACTION

To determine the rate constant for the $N + O_2$ reaction, the concentrations of unreacted nitrogen and oxygen atoms were determined after a known reaction time. All experiments were made at the pressure of 3 mm Hg, and continued for 100 seconds.

Molecular oxygen, at a known flow rate, was admitted to the reaction tube through the top fixed jet, J_1. Nitric oxide was introduced into the gas mixture through the jet, J_2, located 50 cm below the inlet of oxygen, i.e. 50 cm below the fixed jet, J_1. For any given flow rate of nitric oxide, the end point of the nitric oxide 'titration' was obtained and maintained. This measured flow rate of nitric oxide gave an estimation of the nitrogen atom flow rate at the end point, and simultaneously produced an equivalent amount of oxygen atoms. At the same time, it stopped the reaction of active nitrogen with oxygen, by removing all the nitrogen atoms from the gas stream.

Table 2

MAXIMUM YIELDS OF OXYGEN ATOMS FROM THE REACTIONS OF ACTIVE NITROGEN WITH NITRIC OXIDE AND OXYGEN RESPECTIVELY, AT DIFFERENT TEMPERATURES AND AT DIFFERENT LEVELS IN THE REACTION TUBE

Pressure = 2 mm Hg

N_2 Flow rate = 176 x 10^{-6} moles sec^{-1}

O_2 Flow rate = 11.9 x 10^{-6} moles sec^{-1}

Temp. °C	Dist. from fixed jet cm	N + NO Reaction: NO Flow rate moles/sec x 10^6	N + NO Reaction: $(O)_{NO}$ (NO_2 titration) moles/sec x 10^6	N + O_2 Reaction: $(O)_{O_2}$ (NO_2 titration) moles/sec x 10^6	Ratio $(O)_{NO}/(O)_{O_2}$
150	0	2.01	2.03	1.90	1.1
154	10	1.95	1.98	1.92	1.0
153	20	1.91	1.90	1.85	1.0
153	30	1.88	1.86	1.80	1.0
155	40	1.82	1.81	1.79	1.0
152	50	1.79	1.79	1.72	1.0
151	60	1.74	1.76	1.70	1.0
395	0	1.98	2.74	2.97	-
391	10	1.96	2.50	-	-
396	20	1.90	2.34	-	-
398	30	1.86	2.20	-	-
397	40	1.85	2.03	-	-
400	50	1.79	1.90	-	-
401	60	1.76	1.76	1.72	1.0

Table 3

MAXIMUM HYDROGEN CYANIDE PRODUCTION FROM THE REACTION OF ACTIVE NITROGEN WITH ETHYLENE

Temperature = 400°C

Pressure = 1 mm Hg		Pressure = 2 mm Hg	
C_2H_4 Flow rate moles/sec x 10^6	HCN Produced moles/sec x 10^6	C_2H_4 Flow rate moles/sec x 10^6	HCN Produced moles/sec x 10^6
2.52	0.21	3.50	0.86
3.50	0.21	4.50	0.77
5.06	0.24	7.40	0.92
7.60	0.24	10.00	1.00
9.67	0.24	11.30	0.95
		13.90	0.99
		14.50	1.00

Maximum HCN production at 1 mm Hg = 0.24 x 10^{-6} moles sec^{-1}.

Maximum HCN production at 2 mm Hg = 0.98 x 10^{-6} moles sec^{-1}.

Table 4

MAXIMUM YIELDS OF OXYGEN ATOMS FROM THE REACTION OF ACTIVE NITROGEN WITH OXYGEN, ESTIMATED WITH EXCESS NITROGEN DIOXIDE

Distance from fixed jet = 60 cm

Temperature = 400 ± 2°C

Pressure = 1 mm Hg

N_2 Flow rate = 63×10^{-6} moles sec^{-1}

O_2 Flow rate = 11.9×10^{-6} moles sec^{-1}

Max. HCN production = 0.24×10^{-6} moles sec^{-1}

NO 'titration' value = 0.42×10^{-6} moles sec^{-1}

Maximum [O] production moles/sec x 10^6	Ratio $N(HCN)/(O)_{O_2}$	Ratio $N(NO)/(O)_{O_2}$
0.49	0.49	0.85
0.36	0.66	1.16
0.40	0.60	1.05
0.40	0.60	1.05
0.34	0.70	1.23

Pressure = 2 mm Hg

N_2 Flow rate = 176×10^{-6} moles sec^{-1}

O_2 Flow rate = 11.9×10^{-6} moles sec^{-1}

Max. HCN production = 0.98×10^{-6} moles sec^{-1}

NO 'titration' value = 1.76×10^{-6} moles sec^{-1}

Maximum [O] production moles/sec x 10^6	Ratio $N(HCN)/(O)_{O_2}$	Ratio $N(NO)/(O)_{O_2}$
1.55	0.63	1.13
1.55	0.63	1.13
1.60	0.61	1.10
1.63	0.60	1.07
1.67	0.58	1.05
1.60	0.61	1.10

Average $N(HCN)/(O)_{O_2}$ at 1 mm Hg = 0.61 ± 0.05

Average $N(NO)/(O)_{O_2}$ at 1 mm Hg = 1.06 ± 0.10

Average $N(HCN)/(O)_{O_2}$ at 2 mm Hg = 0.61 ± 0.02

Average $N(NO)/(O)_{O_2}$ at 2 mm Hg = 1.09 ± 0.02

Figure 5

HYDROGEN CYANIDE PRODUCTION AS A FUNCTION OF ETHYLENE FLOW RATE, AT 1 mm Hg

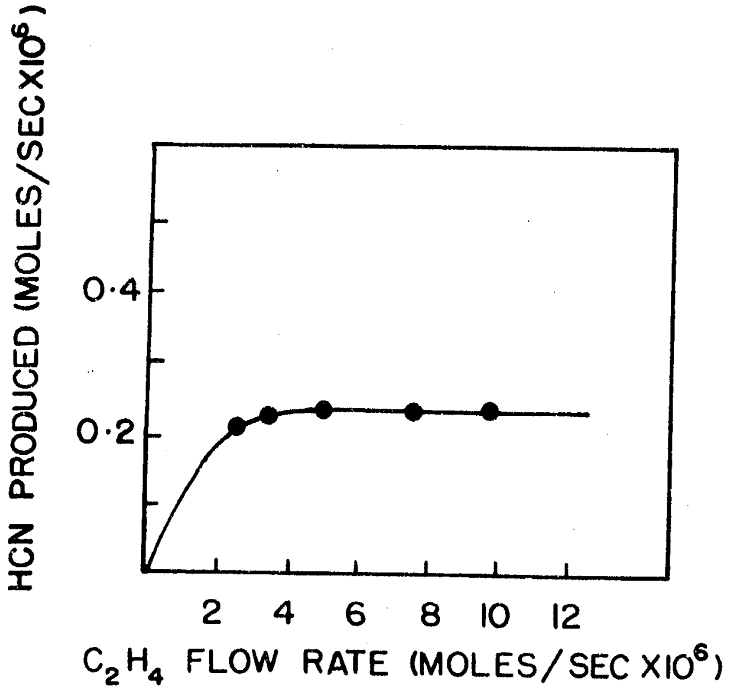
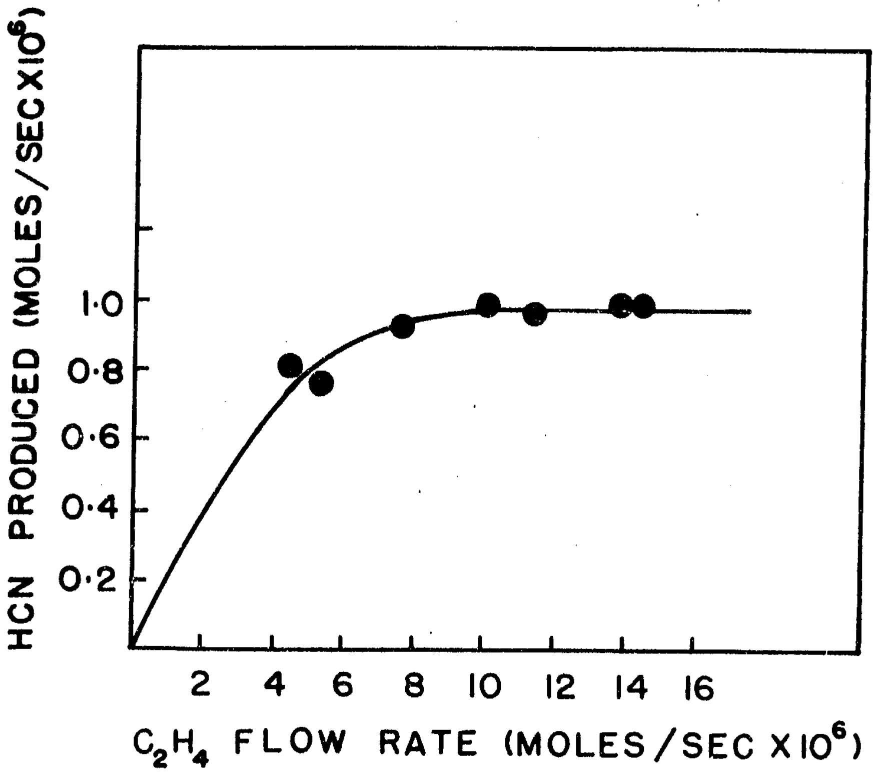

HCN PRODUCED (MOLES/SEC X10^6)
0·4
0·2
2
4
6
8
10
12
C_2H_4 FLOW RATE (MOLES/SEC X10^6)

Figure 6

HYDROGEN CYANIDE PRODUCTION AS A FUNCTION
OF ETHYLENE FLOW RATE, AT 2 mm Hg


HCN PRODUCED (MOLES/SEC X10^6)
1.0
0.8
0.6
0.4
0.2
2
4
6
8
10
12
14
16
C_2H_4 FLOW RATE (MOLES/SEC X10^6)

While the nitric oxide 'titration' was maintained, a considerable excess of nitrogen dioxide was introduced through the jet, J_3, located 5 cm below the point at which nitric oxide was admitted to the system, i.e. 5 cm below the jet, J_2. This allowed an estimation of the <u>total</u> oxygen atom concentration that resulted from the active nitrogen-oxygen reaction, at the top fixed jet, J_1, and from the nitric oxide 'titration' 50 cm below this jet. The oxygen atom concentration at time t (50 cm below the top fixed jet, J_1) was therefore equal to:

$$[O]_t = [O]_{Total} - [O]_{N+NO} = [O]_{Total} - [NO]_t$$

The first step of the reaction of active nitrogen with oxygen can be represented by

$$N + O_2 \xrightarrow{k_1} NO + O \, , \qquad (1)$$

while the much more rapid reaction

$$N + NO \rightarrow N_2 + O \qquad (2)$$

removes the nitric oxide formed in reaction (1).

Other competitive reactions that may be involved in the reaction mixture of active nitrogen with oxygen are:

$$N + N + M \rightarrow N_2 + M \qquad (3)$$

$$N + Wall \rightarrow \tfrac{1}{2}N_2 + Wall \qquad (4)$$

$$O + O + M \rightarrow O_2 + M \qquad (5)$$

$$O + Wall \rightarrow \tfrac{1}{2}O_2 + Wall \qquad (6)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (7)$$

$$N + O + M \rightarrow NO + M \qquad (8)$$

$$NO + O + M \rightarrow NO_2 + M \qquad (9)$$

These reactions are known to cause the disappearance of nitrogen and oxygen atoms to a limited extent (87,146). Reaction (4) may be neglected for the pressure of 3 mm used in the present experiments, since it has been found to be relatively unimportant at pressures higher than about 2.5 mm Hg (127,129). The termolecular reactions (7), (8) and (9) are probably of little significance, compared with the bimolecular processes, (1) and (2); it might be noted, also, that neither nitric oxide, nor nitrogen dioxide, has been found in the reaction products from experiments of short duration (146).

Rate constants were calculated from the data obtained, neglecting reactions (3) to (9), on the assumption that the rate controlling step is reaction (1). The integrated rate equation used for the calculations may be written,

$$k_1 = \frac{2.303}{t[(N)_o - 2(O_2)_o]} \log \frac{(O_2)_o}{(N)_o} \times \frac{(N)_t}{(O_2)_o - (O)_t/2}$$

This was adapted to a fast flow system, with complete mixing, to give the expression

$$k_1 = \frac{2.303\ b^2\ (RT)^2}{[(N)_o - 2(O_2)_o]VP^2} \log \frac{(O_2)_o}{(N)_o} \times \frac{(N)_t}{(O_2)_o - (O)_t/2}$$

where:

k_1 = second order rate constant
$(N)_o$ = initial nitrogen atom flow rate
$(O_2)_o$ = initial oxygen flow rate
$(N)_t$ = nitrogen atom flow rate at time t
$(O)_t$ = oxygen atom flow rate at time t
b = total flow rate
R = gas constant
T = absolute temperature
V = volume of the reaction tube
P = total pressure.

The results for individual experiments, at different temperatures, are given in Table 5. These data gave a satisfactory Arrhenius plot, shown in Fig. 7, from which an activation energy of 7 Kcal/mole was estimated for reaction (1). Extrapolation of the plot to 1/T = 0 gave a value of 3.76×10^{12} cc mole^{-1} sec^{-1} for the pre-exponential factor over the temperature range 453° to 603°K. Accordingly, the rate constant may be written:

$$k_1 = 3.76 \times 10^{12} \exp(-7{,}000/RT)\ \text{cc mole}^{-1}\ \text{sec}^{-1}.$$

Table 5

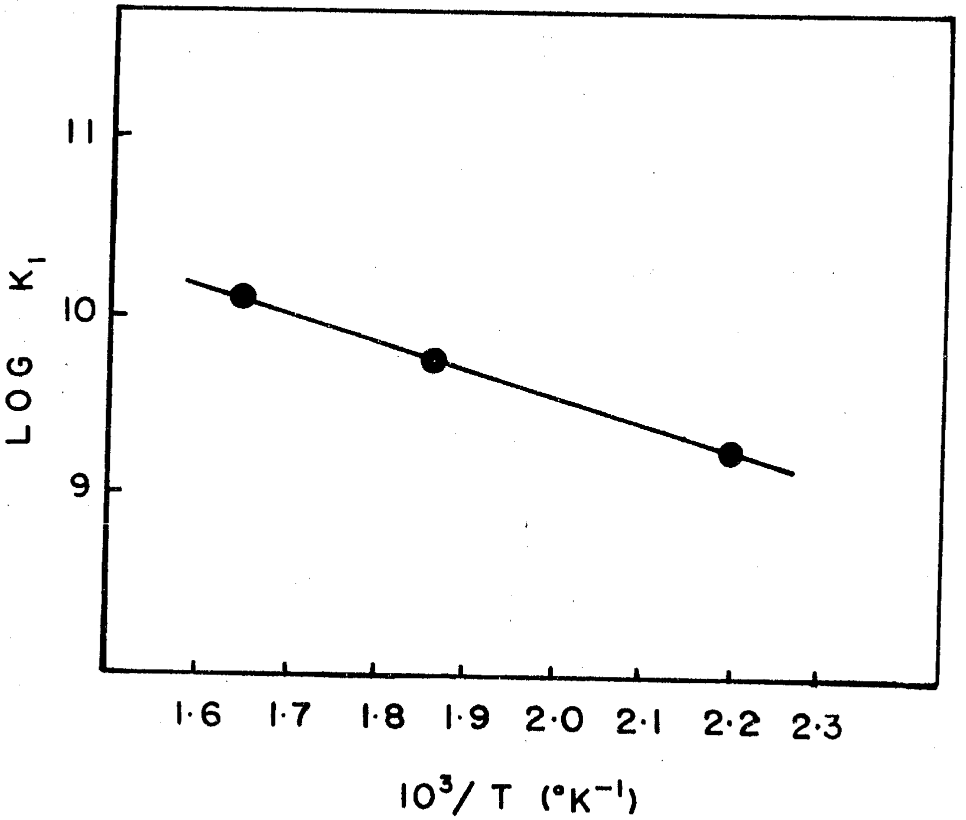
VARIATION OF k_1 AS A FUNCTION OF TEMPERATURE

Pressure = 3 mm Hg
N_2 Flow rate = 352×10^{-6} moles sec^{-1}
$(N)_o$ Flow rate = 3.67×10^{-6} moles sec^{-1}

Temp. °C	$(O_2)_o$ moles/sec x 10^6	$(O)_t$ moles/sec x 10^6	$(N)_t$ moles/sec x 10^6	k_1 cc $mole^{-1}$ sec^{-1}
180	4.01	0.55	2.68	2.09×10^9
180	4.62	0.76	2.65	1.65×10^9
180	4.80	0.78	2.57	1.69×10^9
				Av. 1.81×10^9
265	4.20	1.72	1.74	5.77×10^9
265	4.23	1.55	1.79	5.71×10^9
				Av. 5.74×10^9
335	2.92	1.58	1.87	1.25×10^{10}
330	3.35	1.53	1.47	1.43×10^{10}
330	3.59	1.56	1.61	1.12×10^{10}
				Av. 1.26×10^{10}

Figure 7

ARRHENIUS PLOT OF THE REACTION OF ACTIVE NITROGEN WITH OXYGEN


LOG K$_1$
11
10
9
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
10^3/ T (°K^{-1})

THE EFFECT OF ADDITIVES ON THE NITRIC OXIDE VALUE

Just as the experiments to determine the rate constants for the active nitrogen-oxygen reaction were almost completed, it was observed in the laboratory that, for active nitrogen produced in a condensed electrode discharge, consecutive nitric oxide 'titrations' at intervals over a long period of time, gave decreasing values of the nitrogen atom concentration. For example, a decrease of the 'titration' value from 8 micromoles/sec to 2 micromoles/sec was possible during a five-hour period. After sufficiently long time (4 to 5 hours), the nitrogen atom concentration, as measured by this 'titration', generally attained a steady value. After this value was established, measurement of the nitrogen atom concentration by the maximum hydrogen cyanide production from ethylene showed that the NO/HCN ratio was equal to unity.

These results prompted a study to determine whether the active nitrogen produced by a microwave discharge might behave in a similar manner. If it did, and these were the conditions of the earlier investigations, the NO/HCN ratio might have been unity, and no real discrepancy have existed between the two investigations of the active nitrogen-oxygen reaction by Mavroyannis and Winkler (146), and Clyne and Thrush (87).

With active nitrogen flowing through the reaction vessel, from the microwave discharge, nitric oxide 'titrations' were made at about hourly intervals, at the top fixed jet, J_1. The results, for pressures of 2, 3 and 4 mm Hg, are shown in Table 6, and Fig. 8. Unlike the behaviour with the condensed electrode discharge (136), the results showed no appreciable change, with time, of the nitric oxide 'titration' value.

Since there was no effect of operating time on the nitric oxide 'titration' value, with active nitrogen from a microwave discharge, it seemed desirable to study the possibility that this value might change with the introduction of foreign gases to the system. This effect was also observed by contemporary colleagues in the laboratory, again, with active nitrogen produced in a condensed electrode discharge.

The effect of water vapour was first studied, by pre-mixing it with nitrogen* and passing the mixture into the discharge tube. The 'pink' (Broida) glow was not present in the bulb, V_5, under these conditions. The active nitrogen was then 'titrated', every hour, with nitric oxide at the top fixed jet.

When the active nitrogen concentration was constant, the water supply was stopped to observe how the system behaved. It required only seconds for the system to return to its previous condition. This was easily recognized from the colour intensity of the nitrogen afterglow, and from the return of the

---

*A new grade of nitrogen, 99.995% pure, was used for all the experiments that followed.

'pink' (Broida) glow in the bulb, V_5. The results, thus obtained, at the three pressures are shown in Table 7, and Fig. 9.

The effect of water vapour introduced after the microwave discharge, but before the bulb, V_5, was then studied. The 'pink' (Broida) glow was again quenched in the bulb, V_5. As before, nitric oxide 'titrations' were made, every hour, at the top fixed jet. After two hours of operation of the microwave discharge, the flow of water vapour was stopped, whereupon the 'pink' (Broida) glow returned, almost immediately, to the bulb, V_5, and the yellow afterglow to its original intensity (visual observation). The nitric oxide 'titration' values, at different times, again over the pressure range 2 to 4 mm Hg, are recorded in Table 8, and shown in Fig. 10.

Finally, pure active nitrogen, in the absence of added water vapour, was 'titrated', every hour, with pure nitric oxide, at the top fixed jet. When the nitric oxide 'titration' had achieved a constant value, a mixture of water vapour and nitric oxide was used to 'titrate' the pure active nitrogen, every hour, for the next two hours. Then, pure nitric oxide, without water vapour, was used once again to determine the active nitrogen concentration. The results are shown in Table 9, and Fig. 11.

The observation that the system returned to normal conditions very quickly, after the flow of water vapour, through the discharge, was stopped, suggested that the water was dissociated in the discharge and probably had little influence as a 'poison' against wall recombination. Had there been a real 'poisoning' effect, it might have been expected that, with cessation of the flow of water vapour, the nitrogen atom concentration should have decreased over a considerable period of time, as adsorbed water was removed from the wall of the reaction vessel. On the other hand, if dissociation of the water vapour was extensive, it seemed likely that hydrogen, introduced before the microwave discharge, and possibly oxygen also, should behave in a manner analogous to water vapour added before the discharge. Accordingly, a study was made of the effect, on the nitric oxide 'titration' value, of adding hydrogen and oxygen before the microwave discharge.

Hydrogen, to about the same molar concentration as water, i.e. approximately 0.1×10^{-6} moles/sec, was pre-mixed with nitrogen, prior to their admission to the discharge tube. As with water vapour, the 'pink' (Broida) glow was extinguished in the bulb, V_5. Nitric oxide 'titrations' were made, every hour, at the top fixed jet, until the nitrogen atom concentration remained constant. The hydrogen flow was then stopped. Almost immediately the familiar 'pink' glow became visible again in the bulb, V_5. Water vapour was then introduced, instead of hydrogen, and a nitric oxide 'titration' made. The water vapour was then allowed to pass for one hour, at the end of which time the flow of water was stopped, and a nitric oxide 'titration' again made. The results obtained, at

2, 3 and 4 mm Hg, are shown in Table 10, and Fig. 12.

Similar experiments were made with oxygen, with the results shown in Table 11, and Fig. 13.

NO/HCN RATIO AT THE TOP AND BOTTOM OF THE REACTOR

As indicated previously, no change of the nitric oxide 'titration' value was observed for prolonged periods of continuous operation of the microwave discharge, contrary to the corresponding observations with the condensed electrode discharge (136). On the other hand, Wright *et al*. (72) found the NO/HCN ratio, with the electrode discharge, to decrease, at constant pressure, with time of decay of the active nitrogen in a 'poisoned' system, while in an 'unpoisoned' system the same ratio increased markedly. In view of these observations, it seemed worth while to determine the NO/HCN ratio for a variety of conditions, as above, in the eventuality that some conditions might be found under which this ratio might approach unity. As before, the thought was that, should such conditions be found, they might help to explain the discrepancy between the observations of Mavroyannis and Winkler and of Clyne and Thrush in the oxygen reaction.

Experiments were made, both at the top of the reactor (fixed jet, J_1), and 60 cm below the fixed jet, for different pressures, ranging from 0.75 to 5 mm Hg, at room temperature. The first NO/HCN ratio determination was made after about two hours of continuous operation of the microwave discharge, when

Table 6

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN, AFTER LONG AND CONTINUOUS PERIODS OF OPERATION OF THE MICROWAVE DISCHARGE

Room temperature
Unpoisoned system

Time	NO Flow rate (moles/sec x 10^6)		
hours	Pressure = 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
0	1.18	3.48	4.82
1	1.18	3.36	4.24
2	1.25	3.26	4.21
3	1.18	3.16	3.46
4	-	3.20	3.72
5	-	3.24	3.97
6	-	-	3.87
6.5	-	3.29	-
7.5	-	3.26	-
8.5	-	3.26	-

Figure 8

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN *vs* TIME, AFTER LONG AND CONTINUOUS PERIODS OF OPERATION OF THE MICROWAVE DISCHARGE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg

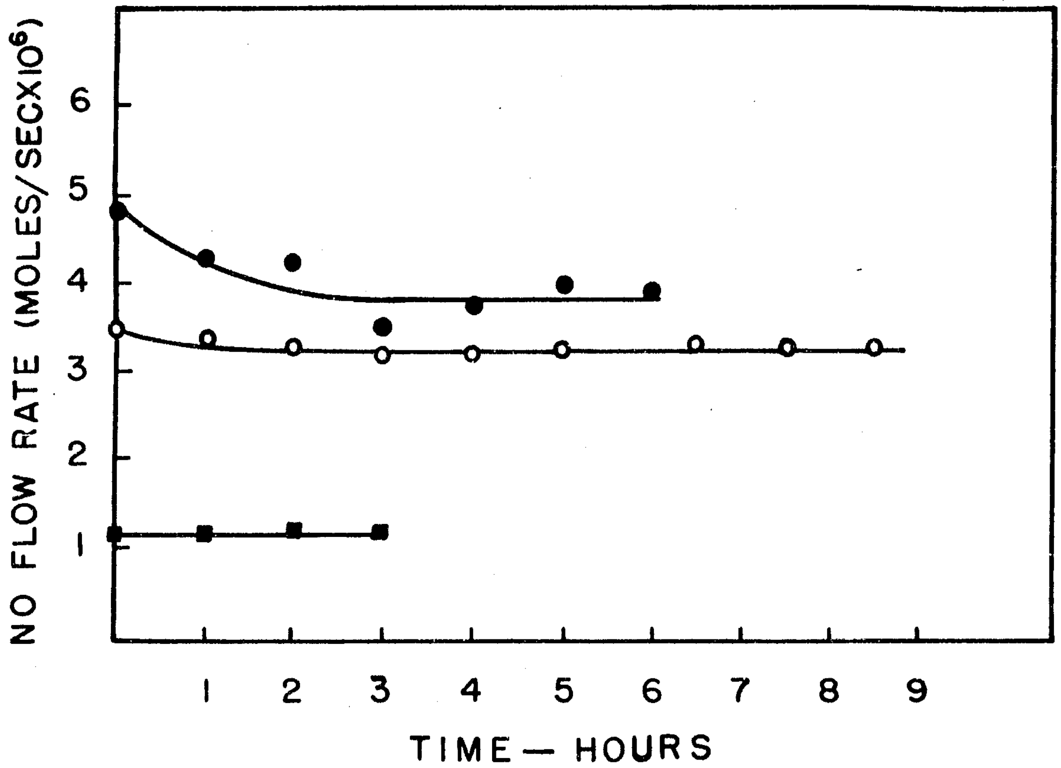

NO FLOW RATE (MOLES/SECX10^6)
1
2
3
4
5
6
TIME — HOURS
1
2
3
4
5
6
7
8
9

Table 7

THE EFFECT OF WATER VAPOUR INTRODUCED BEFORE THE MICROWAVE DISCHARGE

Room temperature

Time	NO Flow rate (moles/sec x 10^6)		
hours	Pressure = 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
0	2.90	4.42	5.26
1	2.81	4.26	4.84
2	2.89	4.34	4.80
Flow of water vapour stopped			
2.25	1.00	2.15	2.99
3	1.04	-	-
3.25	-	2.30	3.00

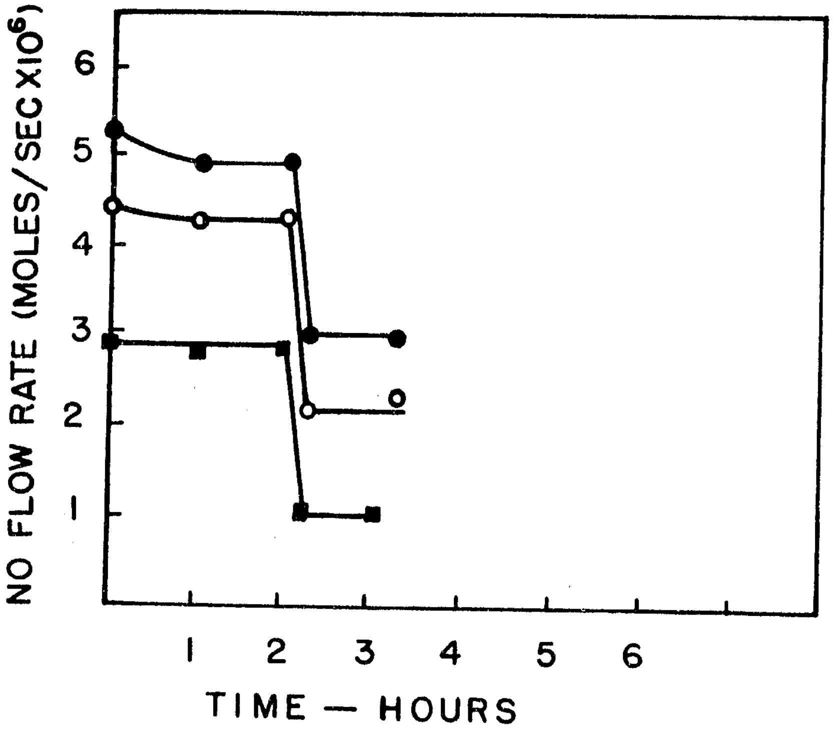
Figure 9

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN *vs* TIME, FOR THE EFFECT OF WATER VAPOUR INTRODUCED BEFORE THE MICROWAVE DISCHARGE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg



NO FLOW RATE (MOLES/SEC X10^6)
6
5
4
3
2
1
1
2
3
4
5
6
TIME — HOURS

Table 8

THE EFFECT OF WATER VAPOUR INTRODUCED AFTER THE MICROWAVE DISCHARGE

Room temperature

Time	NO Flow rate (moles/sec x 10^6)		
hours	Pressure = 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
0	1.46	2.32	3.66
1	1.29	2.02	2.92
2	1.31	2.00	2.95
Flow of water vapour stopped			
2.25	-	1.78	2.67
2.5	0.94	-	-
3.25	-	1.73	2.52
3.5	0.96	-	-

Figure 10

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN *vs* TIME, FOR THE EFFECT OF WATER VAPOUR INTRODUCED AFTER THE MICROWAVE DISCHARGE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg

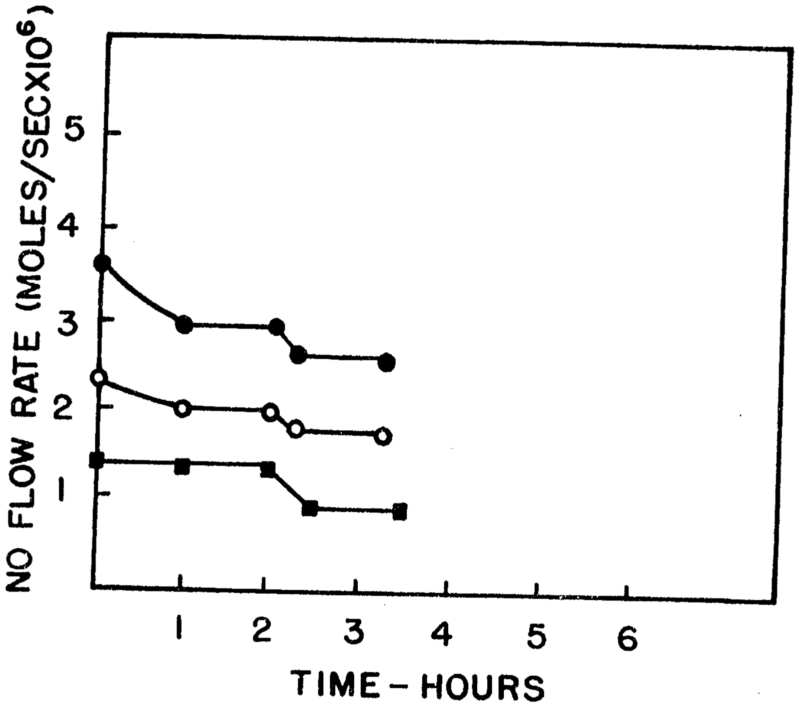

NO FLOW RATE (MOLES/SECX10^6)
5
4
3
2
1
1
2
3
4
5
6
TIME - HOURS

Table 9

THE EFFECT OF WATER VAPOUR PREMIXED WITH NITRIC OXIDE

Room temperature

Time hours	NO Flow rate (moles/sec x 10^6)		
	Pressure= 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
Unpoisoned system			
0	1.22	2.98	3.47
1	1.20	2.68	3.12
2	-	2.46	2.98
3	-	2.65	2.96
Nitric oxide premixed with water vapour			
2	1.35	-	-
3	1.36	-	-
3.25	-	-	3.08
4	-	2.62	-
4.25	-	-	3.09
Flow of water vapour stopped			
3.25	1.22	-	-
4.25	1.20	-	-
5	-	2.64	-
5.25	-	-	3.15

Figure 11

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN *vs* TIME, FOR THE EFFECT OF WATER VAPOUR PREMIXED WITH NITRIC OXIDE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg

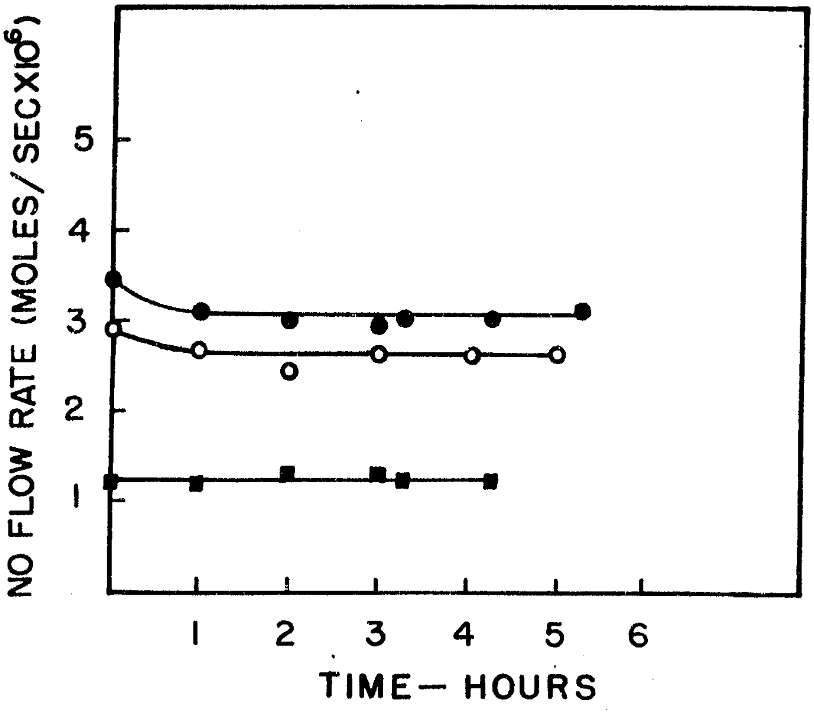

NO FLOW RATE (MOLES/SECX10^6)
1
2
3
4
5
1
2
3
4
5
6
TIME— HOURS

Table 10

THE EFFECT OF HYDROGEN INTRODUCED BEFORE THE MICROWAVE DISCHARGE

Room temperature

Time hours	NO Flow rate (moles/sec x 10^6)		
	Pressure = 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
0	2.86	4.11	4.68
1	-	3.81	4.26
2	2.87	-	-
2.25	-	3.85	4.29
<u>Hydrogen flow stopped</u>			
2.5	1.06	-	-
2.75	-	1.32	2.28
<u>Water vapour introduced</u>			
3.25	-	4.30	4.77
<u>Flow of water vapour stopped</u>			
3.5	-	-	2.45
3.75	-	1.40	-
<u>Water vapour introduced for one hour, its flow then stopped</u>			
4.75	-	1.41	-
6.25	-	1.42	-

Figure 12

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN *vs* TIME, FOR THE EFFECT OF HYDROGEN INTRODUCED BEFORE THE MICROWAVE DISCHARGE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg

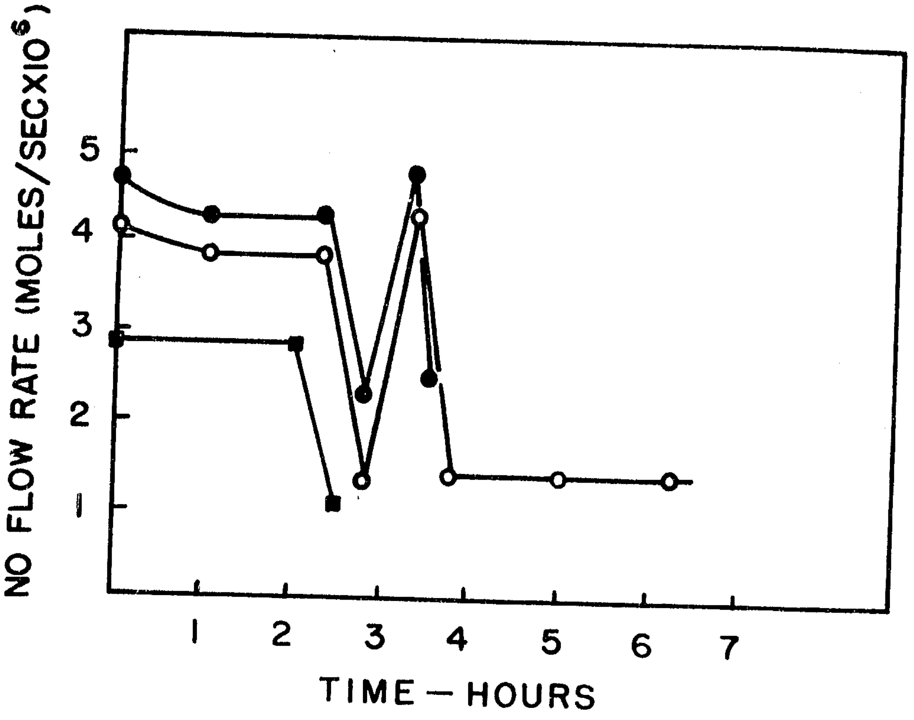

NO FLOW RATE (MOLES/SECX10⁶)
5
4
3
2
1
1
2
3
4
5
6
7
TIME — HOURS

Table 11

THE EFFECT OF OXYGEN INTRODUCED BEFORE THE MICROWAVE DISCHARGE

Room temperature

Time hours	NO Flow rate (moles/sec x 10^6)		
	Pressure = 2 mm Hg	Pressure = 3 mm Hg	Pressure = 4 mm Hg
0	2.30	3.75	4.37
1	2.22	3.48	4.24
2	2.26	3.44	4.15
Flow of oxygen stopped			
2.5	1.11	1.58	2.20
Water vapour introduced			
2.75	-	4.29	4.75
3	2.92	-	-
Flow of water vapour stopped			
3.25	-	1.76	2.45
3.5	1.03	-	-

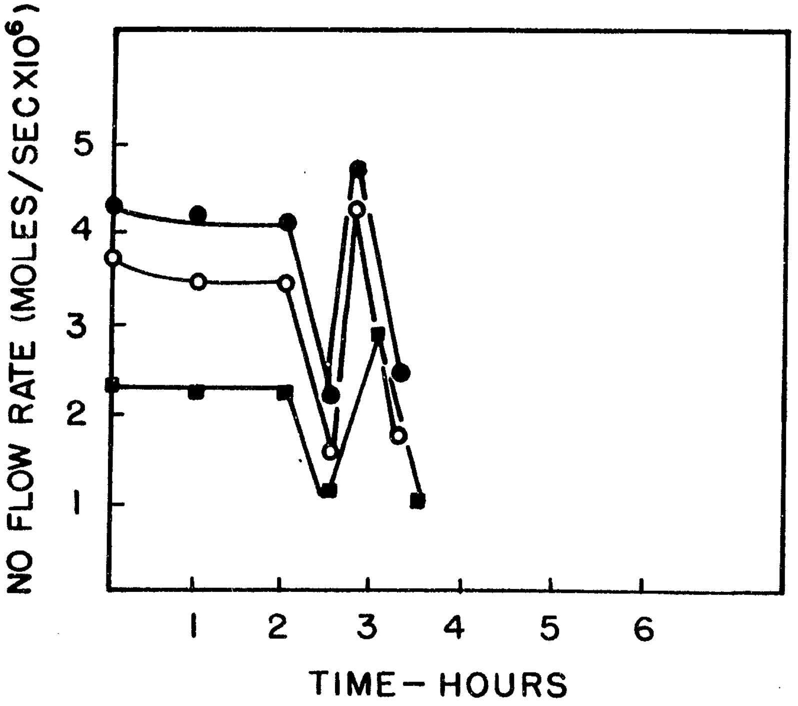
Figure 13

THE NITRIC OXIDE 'TITRATION' VALUE OF ACTIVE NITROGEN vs TIME, FOR THE EFFECT OF OXYGEN INTRODUCED BEFORE THE MICROWAVE DISCHARGE

■ - 2 mm Hg

○ - 3 mm Hg

● - 4 mm Hg


NO FLOW RATE (MOLES/SECX10^6)
1
2
3
4
5
1
2
3
4
5
6
TIME—HOURS

the nitric oxide 'titration' value was constant. There followed, thereafter, any desired number of consecutive experiments.

Nitric oxide 'titrations' were made first, and these were followed by estimations of the maximum hydrogen cyanide production from ethylene for comparable conditions. The hydrogen cyanide produced was trapped in T_2 (Fig. 3), and subsequently titrated as described earlier. The majority of the experiments were made in the 'unpoisoned' system, although a number were made also in a 'poisoned' system (water vapour, approximately 0.1×10^{-6} moles/sec). The results are shown in Table 12, and Figs. 14 and 15.

EXPERIMENTS WITH THE SECOND REACTION VESSEL

In the re-investigation of the active nitrogen-oxygen reaction, outlined in the foregoing discussion, a long tube reactor was used, somewhat analogous to that used by Clyne and Thrush (87), with both their experimental techniques, and those of Mavroyannis and Winkler (146). The values for the maximum oxygen atom production, by both methods, were in good agreement with the nitric oxide 'titration' value of the active nitrogen, i.e. in agreement with the results of Clyne and Thrush. Also, no experimental conditions could be found such that the extent of reaction, whether measured by the NO or C_2H_4 reactions, would be the same $(\frac{NO}{HCN} \approx 1)$. Rather clearly, therefore, the discrepancy between the earlier studies by Clyne and Thrush, on one hand, and of Mavroyannis and Winkler on the other had to be sought in some other factor that depended upon the different types of reactor

Table 12

THE NO/HCN RATIO AT THE TOP AND BOTTOM OF THE REACTOR

Room temperature

Top of the reactor (Fixed jet, J_1)			Bottom of the reactor (60 cm below fixed jet)		
NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN	NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN
A. UNPOISONED SYSTEM					
		Pressure = 0.75 mm Hg			
0.11	0.065	1.69	-	-	-
0.10	0.065	1.54	-	-	-
		Av. 1.61			
		Pressure = 1 mm Hg			
0.24	0.14	1.71	0.34	0.18	1.82
0.25	0.14	1.78	0.29	0.16	1.81
0.27	0.15	1.80	0.28	0.16	1.75
		Av. 1.76			
-	-	-	0.29	0.16	1.81
					Av. 1.79
		Pressure = 2 mm Hg			
1.07	0.58	1.84	1.03	0.54	1.90
1.03	0.56	1.83	0.95	0.52	1.83
1.10	0.58	1.89	0.95	0.52	1.83
		Av. 1.85			Av. 1.85

/Contd.

Room temperature

Top of the reactor (Fixed jet, J_1)			Bottom of the reactor (60 cm below fixed jet)		
NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN	NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN
		Pressure = 2.5 mm Hg			
1.42	0.64	2.21	1.18	0.54	2.18
1.40	0.64	2.19	1.23	0.56	2.19
		Av. 2.20			Av. 2.18
		Pressure = 3 mm Hg			
2.18	1.00	2.18	1.58	0.68	2.32
2.11	0.96	2.19	1.60	0.72	2.22
2.04	0.96	2.12	1.53	0.68	2.25
		Av. 2.16			Av. 2.26
		Pressure = 4 mm Hg			
2.96	1.34	2.20	2.15	0.96	2.23
3.00	1.36	2.20	2.10	0.96	2.18
2.88	1.32	2.18	2.00	0.96	2.08
					Av. 2.16
2.88	1.32	2.18	-	-	-
2.94	1.32	2.22	-	-	-
2.94	1.32	2.22	-	-	-
		Av. 2.20			

/Contd.

Room temperature					
Top of the reactor (Fixed jet, J_1)			Bottom of the reactor (60 cm below fixed jet)		
NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN	NO Flow rate moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN
		Pressure = 5 mm Hg			
3.10	1.34	2.31	-	-	-
3.02	1.34	2.25	-	-	-
		Av. 2.28			
B. POISONED SYSTEM					
		Pressure = 0.75 mm Hg			
0.58	0.35	1.65	-	-	-
0.60	0.37	1.62	-	-	-
		Av. 1.63			
		Pressure = 2 mm Hg			
2.84	1.48	1.91	-	-	-
2.81	1.48	1.89	-	-	-
		Av. 1.90			
		Pressure = 3 mm Hg			
4.25	1.96	2.16	-	-	-
4.22	1.94	2.17	-	-	-
		Av. 2.16			

Figure 14

PLOT OF THE NO/HCN RATIO *vs* PRESSURE

'Unpoisoned' system

● - Fixed jet

▲ - 60 cm below fixed jet

'Poisoned' system

■ - Fixed jet

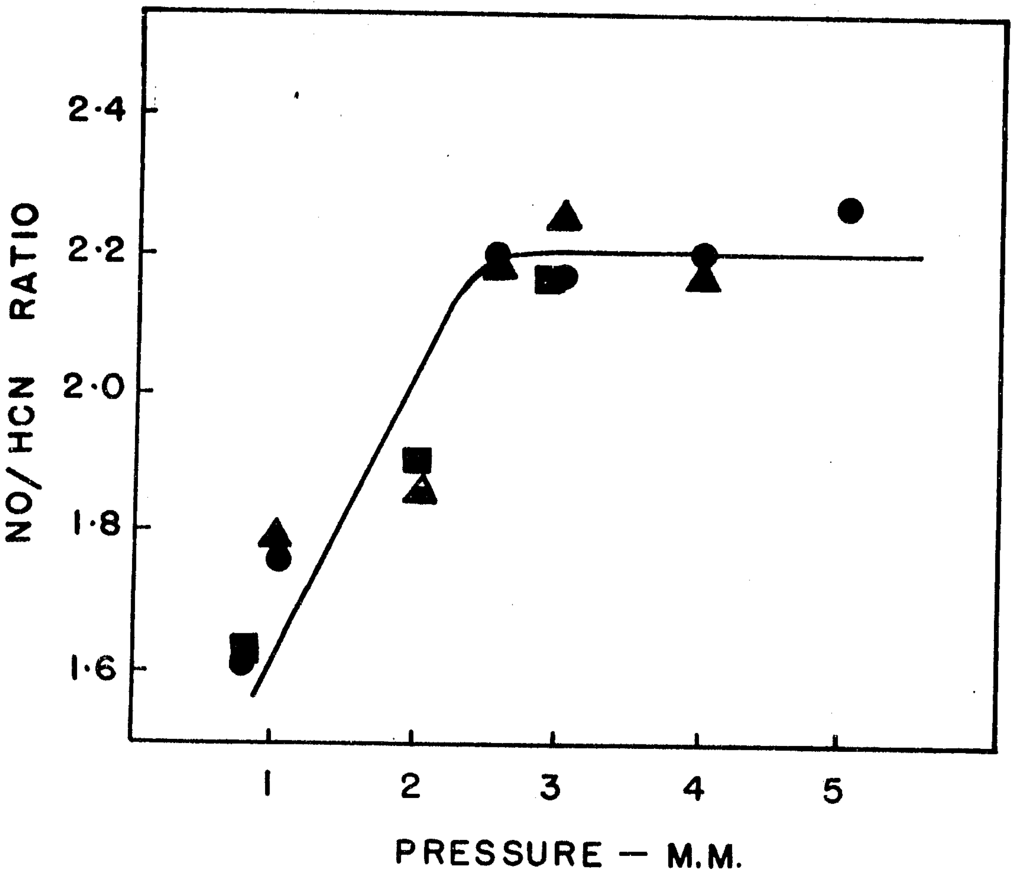

2·4
2·2
2·0
1·8
1·6
NO/HCN RATIO
1
2
3
4
5
PRESSURE — M.M.

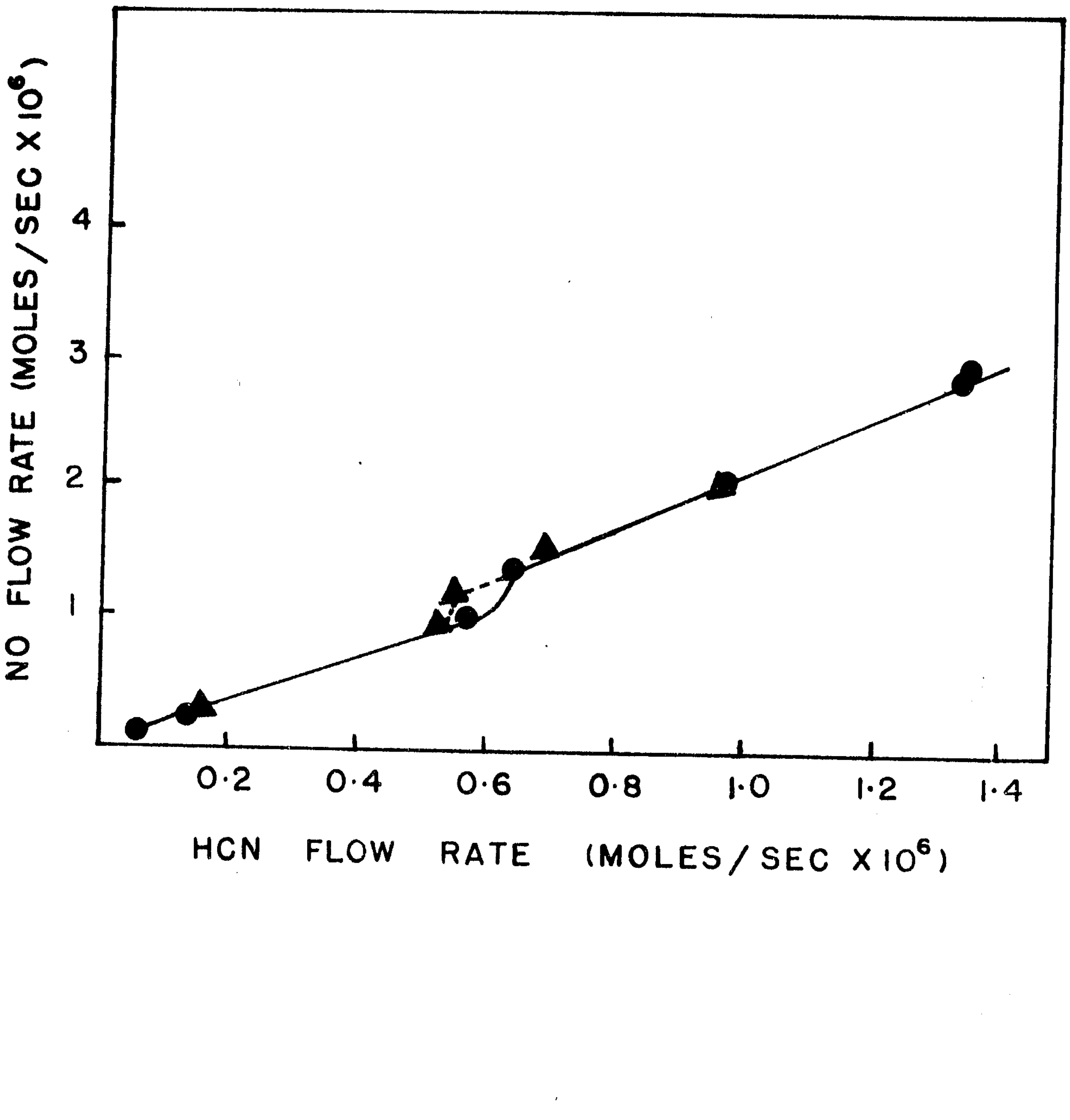
Figure 15

PLOT OF THE NITRIC OXIDE 'TITRATION' VALUE
vs MAXIMUM HYDROGEN CYANIDE PRODUCTION

'Unpoisoned' system

● - Fixed jet

▲ - 60 cm below fixed jet



NO FLOW RATE (MOLES/SEC X 10^6)
1
2
3
4
0·2
0·4
0·6
0·8
1·0
1·2
1·4
HCN FLOW RATE (MOLES/SEC X 10^6)

used. Accordingly, the rather obvious next step in the investigation was to construct a reaction vessel, as identical as possible with that used by Mavroyannis and Winkler (see Fig. 4), to determine whether their observations could be substantiated.

A reactor of M-W type* was constructed, as illustrated in Fig. 4, and connected, through K, to the discharge tube, and through L, to that part of the system that led to the traps T_2 and T_3. When the system was put into operation, with nitric oxide introduced through jet A, a difficulty was encountered in obtaining the dark point of the N + NO reaction. Owing to a high linear velocity, the dark point was observed in the neighbourhood of the traps, instead of inside the reaction tube. The same behaviour was observed for the active nitrogen-oxygen reaction. This meant that active nitrogen was present around the jet, E, through which it was intended to add nitrogen dioxide for the estimation of the oxygen atom concentration from the reaction. Since active nitrogen reacts with nitrogen dioxide (73,74,86,130,131), to produce some nitric oxide, the

---

*To avoid any confusion, since a rather large number of different reactors were used, the following notation was adopted: The long reaction tube with the movable jets will be designated as 'reactor I'; the reactor used by Mavroyannis and Winkler (146) will be referred to as 'M-W reactor', and its modifications as 'M-W reactor', followed by an identifying comment on the type of modification.

results would have been unreliable. It was found that throttling the pump, to decrease the linear velocity, made it possible to circumvent this uncertainty, by causing the dark point to retreat to a point close to the jet, A.

Experiments were first made with this system (M-W reactor), by admitting oxygen into the active nitrogen stream through the jet, A. The maximum oxygen atom production was then determined by introducing an excess of nitrogen dioxide through the jet, E, located 23.5 cm below the jet, A, and analysing the trapped N_2O_3 as described earlier. At the same time, a nitric oxide 'titration' was made, to determine the nitrogen atom concentration at the jet, A. Analogous experiments were made with ethylene. Ethylene was admitted to the reaction tube through jet, A, and the maximum hydrogen cyanide production, for high reactant flow rates, was determined in the usual way. The results at the pressures of 3, 4 and 5 mm Hg, and about 400°C, are shown in Table 13.

The maximum oxygen atom production was now in agreement with the maximum yield of hydrogen cyanide, i.e. in agreement with the results of Mavroyannis and Winkler (146), rather than with the nitric oxide 'titration' value of active nitrogen. It was apparent that some factor was present with this system, such that the results were shifted towards the hydrogen cyanide value. Further investigation was therefore directed towards the identification of that factor, achievement of which would resolve the problem under investigation.

It seemed worth while to determine, first, whether an impurity (e.g. hydrogen), introduced before the microwave discharge, might reveal any suggestive behaviour of the active nitrogen-oxygen reaction in this system. However, no effect on the results was observed in any of the experiments,that were made, as indicated in Table 13.

The possible effect of inserting a 300 cc bulb between the discharge tube and the M-W reactor was next investigated, since such a volume was present in experiments that had been made with reactor I. Again, no such effect was observed.

A modification of the M-W reactor was constructed, in which only two fixed jets, corresponding to A and E, were present. These were 23.5 cm apart, and pointed upstream, to introduce reactant countercurrent to the active nitrogen stream. Experiments were then made as with the M-W reactor. In two of these, the length of the reactor was changed. This was done, first, by sealing a pyrex tube, 45 cm long and 26 mm I.D., to the inlet end of the reaction tube, so that its entire length was somewhat analogous to that of reactor I, while for another series of experiments, it was further lengthened with a tube, 20 cm long and 26 mm I.D., sealed to the exit end. The results of studies made with these modified reactors are shown in Table 13.

It was noted that when the volume of the reactor below the inlet for nitrogen dioxide was increased, the results obtained by analysis with excess nitrogen dioxide were shifted towards the values obtained by the nitric oxide 'titration'. It was suspected, therefore, that the analytical method used by Mavroyannis and Winkler, in which N_2O_3 is trapped, might have been deficient under some conditions.

Further check on the validity of the method was therefore made, by passing molecular nitrogen through the system, with no discharge, and introducing a known amount of nitric oxide into the reactor through the jet, A. Excess nitrogen dioxide was then admitted, as before, through the jet, E, and the N_2O_3 produced was trapped and estimated in the usual way. Surprisingly enough, the analytical method was found to be only 82.4% efficient.

In view of these last results, a M-W reactor (Fig. 4) was again incorporated into the system, and the analytical procedure based on excess nitrogen dioxide was again checked by the same experimental procedure. The results now indicated that the efficiency of the method was drastically reduced, to 64%.

It seemed possible that this grossly reduced efficiency of the analytical method might have resulted from the throttling that was used, as indicated earlier, to contain the dark end-point of the nitric oxide 'titration' within the reactor, when the shorter reactors replaced the reactor I used in the initial experiments. It may be recalled that tests of the analytical method gave satisfactory results for the un-throttled flow through the reactor I (Table 1, p. 55). Accordingly, the reactor I, used initially, was again put into place, and nitric oxide, at a known flow rate, was introduced into the reaction vessel at three different levels, through the movable jet. Experiments were made with throttled flow, at a constant pressure. Analyses were made with an excess of nitrogen dioxide admitted to the reactor through the jet, J_3, located 65 cm below the top fixed jet (Fig. 3). The results showed that the analytical method was satisfactory, regardless of the extent of throttling, and of the level at which nitric oxide was admitted to the reactor.

Yet another reactor was then put into place. This consisted of a M-W reactor, except that a tube, 30 cm long and 28 mm I.D., was sealed to the exit end. This additional tube was of such dimensions that the volume below the inlet of nitrogen dioxide was approximately the same as that for the reactor I. The results, with additions of nitric oxide as above, now showed that the analytical method was entirely satisfactory.

In calculating the volume to be added below the nitrogen dioxide inlet, for the previous experiment, the volume contained in the B 40 ground joint at the bottom of reactor I (Fig. 3) was included. As a variant of the last experiment, described above, the reactor I was again placed in the system and the volume in the ground joint filled with di-butyl phthalate. Experiments showed that this volume was not essential to satisfactory application of the analytical method.

Further to the above extensive comparisons between the two kinds of reactors, there remained a relatively minor difference to be examined, namely the type of jets. A reaction vessel was therefore constructed, as a modification of the M-W reactor, with two bulb jets, A and E, instead of tapered inlet jets. Four fine holes were located symmetrically around the peripheries of the bulbs. The volume below the inlet for nitrogen dioxide was the same as in reactor I when the volume of the B 40 ground joint was excluded. The results showed that the analytical method was efficient, and required some 100-120 cc less volume below the inlet for nitrogen dioxide, than with the tapered inlet jets.

The results for all the experiments designed to test the efficiency of the analytical method under the variety of conditions are contained in Table 14. They left little doubt that oxygen atom production in the active nitrogen-oxygen reaction could be analysed reliably by the method based on adding an excess of nitrogen dioxide only if sufficient volume is available, after the nitrogen dioxide is added, to permit the $NO + NO_2$ reaction to go to completion.

RATE CONSTANTS FOR THE $NO + NO_2$ REACTION

In view of the conclusion enunciated above, it seemed worth while to obtain some idea of the rate constant for the $NO + NO_2$ reaction, since there seemed to be an opportunity to

Table 13

MAXIMUM YIELD OF HYDROGEN CYANIDE AND OXYGEN ATOMS FROM THE REACTIONS OF ACTIVE NITROGEN WITH ETHYLENE AND OXYGEN RESPECTIVELY, AT VARIOUS PRESSURES

Temperature = 400 ± 2°C

O_2 Flow rate = 11.9×10^{-6} moles sec^{-1}

NO Flow rate moles/sec x 10^6	Maximum [O] Production moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN	Ratio NO/O	Ratio HCN/O
M-W reactor (Permanent throttling with capillary)					
		Pressure = 3 mm Hg			
0.46	0.26	0.235	1.95	1.76	0.9
		Pressure = 4 mm Hg			
0.80	0.44	0.45	1.80	1.82	1.0
		Pressure = 5 mm Hg			
1.23	0.67	0.68	1.80	1.83	1.0

/Contd.

Temperature = $400 \pm 2^{\circ}C$
O_2 Flow rate = 11.9×10^{-6} moles sec^{-1}

NO Flow rate moles/sec x 10^6	Maximum [O] Production moles/sec x 10^6	Maximum HCN Production moles/sec x 10^6	Ratio NO/HCN	Ratio NO/O	Ratio HCN/O
Introduction of hydrogen (0.1×10^{-6} moles sec^{-1}) before the microwave discharge					
		Pressure = 3 mm Hg			
1.0	0.67	0.62	1.60	1.50	0.92
		Pressure = 4 mm Hg			
1.58	0.89	0.93	1.70	1.77	1.05
		Pressure = 5 mm Hg			
2.02	1.16	1.18	1.70	1.74	1.0
M-W reactor, two jets countercurrent (Permanent throttling without capillary)					
		Pressure = 5 mm Hg			
1.65	0.80	0.85	1.94	2.06	1.06
		Pressure = 2 mm Hg			
1.23	0.67	0.67	1.83	1.83	1.0
1.26	0.67	0.68	1.85	1.88	1.0
Elongation at the inlet end					
1.28	0.67	0.69	1.85	1.90	1.0
Elongation at the exit end					
1.2	0.91	0.68	1.76	1.31	0.74

Table 14

EXPERIMENTS CONCERNING THE TRAPPING EFFICIENCY OF NITRIC OXIDE, BY USING EXCESS NITROGEN DIOXIDE, IN DIFFERENT SYSTEMS

Known NO moles/sec x 10^6	Trapped NO moles/sec x 10^6	Efficiency %
M-W reactor, two jets countercurrent		
0.89	0.71	79.8
1.16	0.94	81.0
1.45	1.25	86.2
		Av. 82.4
Correction factor = 1.21		
M-W reactor		
0.80	0.49	61
1.19	0.80	67
		Av. 64
Correction factor = 1.56		
Reactor I		
NO introduced 60 cm below fixed jet		
0.82	0.80	97.6
1.18	1.16	98.3
NO introduced 40 cm below fixed jet		
1.19	1.16	97.5
NO introduced through the fixed jet		
1.79	1.78	99.4
M-W reactor elongated at the exit end, tapered jets		
1.24	1.21	97.6
Reactor I, ground joint filled with di-butyl phthalate		
1.26	1.25	99.2
M-W reactor elongated at the exit end, bulb jets		
1.17	1.12	96

do this with relatively simple alterations to the equipment and procedures that were being used.

Although it appears that the existence of dinitrogen trioxide (N_2O_3) in the liquid phase has been accepted, its stability as a gas was, for some time, controversial [cf. review by Beattie (162)]. However, its existence as a stable compound in the gas phase has been demonstrated by measurements of the equilibrium constant for the reaction (157,163,164),

$$NO + NO_2 \overset{k}{\rightleftharpoons} N_2O_3 \ . \qquad (10)$$

Its Raman (165) and ultraviolet (166) spectra have also been recorded.

The kinetics of the exchange of nitrogen between nitric oxide and nitrogen dioxide in the reaction

$$N^{14}O + N^{15}O_2 \rightleftharpoons N^{15}O + N^{14}O_2$$

was examined by Leifer (167) in the gas phase, at a total pressure of 2.5 cm Hg and temperature -35°C. A lower limit for the rate constant was 10^6 cc mole^{-1} sec^{-1}. The observed equilibrium constant at 25°C was 0.96 ± 0.02, compared with a value of 0.967 calculated from spectroscopic data.

To determine the rate constant for reaction (10), nitrogen dioxide was added to a stream of nitric oxide and molecular nitrogen, and the N_2O_3 trapped, and estimated, after a known reaction time.

The reaction vessel used in this series of experiments was the M-W reactor with two bulb jets. Nitric oxide, at a known flow rate, was introduced through the jet, A, into a stream of molecular nitrogen. Nitrogen dioxide, at the rate of 10^{-5} moles/sec, was admitted to the reaction tube through the jet, E, located 23.5 cm below the inlet of nitric oxide. Different reaction times were attained, by changing the volume from the inlet for nitrogen dioxide to the level of the liquid air surrounding the trap. The reaction was stopped at the level of liquid air, at which point the N_2O_3 was trapped, and subsequently estimated. Experiments were made at a pressure of 3.3 mm Hg, with gas flows that continued for 120 seconds. The results obtained, for different reaction times, are shown in Table 15.

'Blank' experiments showed that, when nitric oxide was passed through the trap, immersed in liquid air, for 120 seconds, under the same conditions as those used for the rate constant determination, no trace of nitric oxide was trapped. Hence, for conditions of incomplete consumption of nitric oxide the results would not be rendered inaccurate by contamination of the N_2O_3 with condensed nitric oxide.

It was also observed that, if nitrogen dioxide, of an amount equal to that used in the rate constant determinations, was condensed into the trap, and a known amount of nitric oxide also passed through the trap, no nitric oxide was retained.

The reaction leading to the formation of N_2O_3 may be assumed to be of second order. Hence, by using a considerable excess of nitrogen dioxide, compared with the flow rate of nitric oxide, the reaction may be reduced to a pseudo-first order reaction (168). The rate expression is given by

$$\frac{d(N_2O_3)}{dt} = k(NO)(NO_2)$$

In the present experiments, $(NO_2)_o \simeq 10(NO)_o$, where $(NO)_o$ and $(NO_2)_o$ represent initial flow rates.
Hence,

$$\frac{d(N_2O_3)}{dt} \cong k(NO_2)_o(NO) = k'(NO) ,$$

and

$$k = \frac{k'}{(NO_2)_o} ,$$

where k' = pseudo-first order rate constant
and k = second order rate constant.
By integration of the pseudo-first order equation,

$$k' = \frac{1}{t} \ln \frac{(NO)_o}{(NO)_o - (N_2O_3)_t} .$$

When $\ln (NO)_o/(NO)_o - (N_2O_3)_t$ was plotted against t, a straight line was obtained (Fig. 16), the slope of which was the pseudo-first order rate constant k'. The value so obtained was:

$$k' = 12.8 \text{ sec}^{-1} .$$

Accordingly, a value for the second order rate constant k was estimated, based on the known value of k'. Its value was:

$$k = 1.3 \times 10^{9} \text{ cc mole}^{-1} \text{ sec}^{-1} \quad .$$

Table 15

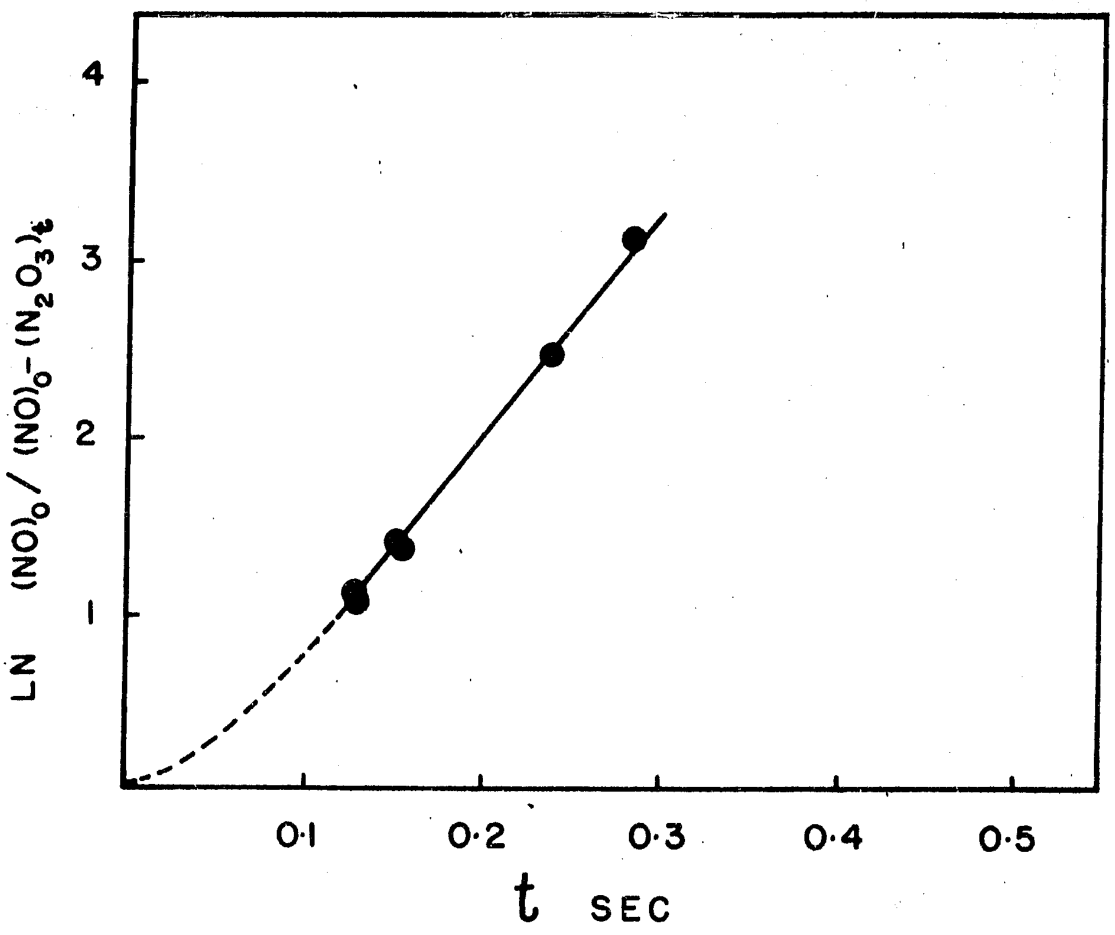
DATA FOR THE CALCULATION OF THE RATE CONSTANTS k' AND k

Temperature = 30°C
Pressure = 3.3 mm Hg
N_2 Flow rate = 125×10^{-6} moles sec^{-1}
$(NO_2)_o$ Flow rate = 10×10^{-6} moles sec^{-1}

Reaction Volume cm^3	Reaction Time sec.	$(NO)_o$ Flow rate moles/sec x 10^6	$(N_2O_3)_t$ Produced moles/sec x 10^6	$\ln \frac{(NO)_o}{(NO)_o - (N_2O_3)_t}$
100	0.128	1.17	0.76	1.048
100	0.128	1.05	0.71	1.127
120	0.154	1.19	0.89	1.377
120	0.154	0.97	0.71	1.316
185	0.238	1.18	1.08	2.468
220	0.283	1.17	1.12	3.152

Figure 16

PLOT OF $\ln (NO)_o/(NO)_o - (N_2O_3)_t$ vs t



4
3
2
1
LN (NO)₀ / (NO)₀ − (N₂O₃)ₜ
0·1
0·2
0·3
0·4
0·5
t SEC

DISCUSSION

Discussion of the results of the present study may be focussed, almost entirely, on one important question: Has a reasonable explanation been found for the discrepancy, outlined earlier, between the results obtained by Clyne and Thrush, and those of Mavroyannis and Winkler, for the active nitrogen-oxygen reaction? To answer this question, it would seem useful, even necessary, to recapitulate briefly the nature of the discrepancy, and the steps taken to resolve it. Only in this way does it seem possible to present the basis for the conclusion finally reached, in such a way that its correctness may be readily assessed. This will involve, inevitably, some repetition. However, it will be possible, at the same time, to comment on a number of interesting observations that have been made during the course of the study.

It will be recalled that the discrepancy resided in a marked disagreement on the maximum extent to which the reaction may occur, relative to the maximum extent to which active nitrogen may destroy nitric oxide, or may react with ethylene to form hydrogen cyanide. Mavroyannis and Winkler had analysed for the production of oxygen atoms in the active nitrogen-oxygen reaction by adding an excess of nitrogen dioxide, which permitted an equivalent amount of nitric oxide to be trapped as N_2O_3, according to the sequence,

$$N + O_2 \rightarrow NO + O$$

$$N + NO \rightarrow N_2 + O$$

$$O + NO_2 \rightarrow NO + O_2$$

$$NO + NO_2 \rightarrow N_2O_3$$

They found that the $N + O_2$ reaction appeared to take place to an extent which corresponded remarkably well, over a range of pressures, with the maximum production of hydrogen cyanide from ethylene, when it reacted with active nitrogen formed under comparable conditions. They were aware, from the data of Verbeke and Winkler, that this maximum hydrogen cyanide yield was generally less than the corresponding extent to which nitric oxide might be decomposed (the NO/HCN ratio being of the order 1.4 to 2.4), and concluded that the good agreement between the maximum extents of the oxygen and ethylene reactions supported the maximum hydrogen cyanide yield from the ethylene reaction, rather than the extent of nitric oxide destruction, as a measure of the active nitrogen concentration.

Subsequently, however, Clyne and Thrush compared the extent to which nitric oxide was decomposed by active nitrogen, inferred from the nitric oxide gas-phase 'titration', with the extent of oxygen atom production in the oxygen reaction, determined also by a gas-phase 'titration', but with nitrogen dioxide. They found excellent agreement between these two quantities, which gave strong support to the nitric oxide 'titration' as a method for estimating the nitrogen atom concentration in active nitrogen.

Clearly, further study of the oxygen reaction was necessary to establish, if possible, the reason for the quite different results obtained in the two studies, and, as indicated earlier, the present study was undertaken with this end in view.

A logical first step in attempting to trace the source of the discrepancy was, of course, to re-investigate the oxygen reaction, with particular attention to the difference in analytical methods previously used for estimating the oxygen atom production in the reaction. To this end, a long-tube reactor was first constructed (reactor I of the preceding presentation of data), somewhat analogous to that used by Clyne and Thrush. The maximum yields of oxygen atoms from the reactions of active nitrogen with nitric oxide and with oxygen were compared, at different levels in the reactor, using the nitrogen dioxide 'titration' procedure. The data obtained at 150°C showed excellent correspondence between these values (Table 2). At 400°C, this correspondence was no longer obtained, but it was possible to demonstrate that, at the higher temperature, thermal decomposition of nitrogen dioxide (169,170) rendered the nitrogen dioxide 'titration' unreliable for estimating the oxygen atom concentrations. It was concluded, therefore, that the data from these experiments were in good agreement with those of Clyne and Thrush (87), who reported that oxygen and nitric oxide reacted with active nitrogen to the same extents. In other words, the data could be interpreted as corroborating the nitric oxide 'titration' method as a measure of the nitrogen atom concentration.

There then followed a comparison, at 400°C in the same reactor, of the maximum oxygen atom production from the active nitrogen-oxygen reaction, as measured by the excess nitrogen dioxide method, with the maximum yield of hydrogen cyanide from the active nitrogen-ethylene reaction. Although the experimental techniques were similar to those of Mavroyannis and Winkler (146), the maximum yields of oxygen atoms from the oxygen reaction (Tables 3 and 4 and Figs. 5 and 6) did not agree with the maximum yields of hydrogen cyanide, as these authors had found previously. Instead, they were again in good agreement with the nitric oxide 'titration' value for active nitrogen, i.e. in agreement with the previous observations, and with the results of Clyne and Thrush (87). Again, the nitric oxide 'titration' method for determining nitrogen atom concentrations appeared to be confirmed in its validity.

Other experiments in the same reactor made it possible to obtain rate constants for the reaction of active nitrogen with molecular oxygen, and thereby permitted a comparison with the earlier studies on the basis of rates, rather than yields. It was assumed that the mechanism of the reaction was

$$N + O_2 \xrightarrow{k_1} NO + O \qquad \Delta H^o = -32.8 \text{ kcal/mole}^*$$

---

*ΔH^o calculated from data given in Ref. 33, Table 39.

followed by the fast reaction

$$N + NO \rightarrow N_2 + O \qquad \Delta H^\circ = -75.1 \text{ kcal/mole.}$$

The data (Table 5 and Fig. 7) yielded a rate constant given by

$$k_1 = 3.76 \times 10^{12} \exp(-7{,}000/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

over the temperature range 453° to 603°K. This may be compared with the other values reported in the literature, as follows:

$$k_1 = 2 \times 10^{12} \exp(-6{,}200/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

(Kistiakowsky and Volpi - Ref. 86)

$$k_1 = 1.7 \times 10^{13} \exp(-7{,}500/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

(Kaufman and Decker - Ref. 145)

$$k_1 = 2.3 \times 10^{12} \exp(-5{,}900/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

(Mavroyannis and Winkler - Ref. 146)

$$k_1 = 8.3 \times 10^{12} \exp(-7{,}100/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

(Clyne and Thrush - Ref. 87)

The value for the rate constant obtained in the present investigation may be considered to be in quite good agreement with most of the previous results, in view of the different experimental techniques used. However, it may be considered significant that it is in particularly good agreement with the value reported by Clyne and Thrush, and less satisfactorily with the value found by Mavroyannis and Winkler, even though the present value was determined by using their analytical method to measure oxygen atom concentrations (i.e. addition of excess nitrogen dioxide).

All of the experiments made in the long tube reactor, as above, yielded data in support of the study made previously by Clyne and Thrush without, however, giving any indication of the reason for the discrepancy between their work and that of Mavroyannis and Winkler. It became apparent that this was likely to be found only by adopting some other approach to the problem.

Simultaneously with the present study, it was observed in this laboratory that, when active nitrogen was produced by a condensed discharge between electrodes, the nitric oxide 'titration' value dropped as the discharge was operated continuously over long periods. After 4 to 5 hours, it might reach a steady value, such that the NO/HCN ratio approached unity.

This behaviour suggested that consideration should be given to the possibility that a similar behaviour might be observed with active nitrogen produced by a microwave discharge. If this were true, the experiments of Clyne and Thrush might have been made for conditions such that the NO/HCN ratio, had it been determined, might have been unity. No real discrepancy would then have existed, for their experiments, in the comparative maximum extents of the oxygen, nitric oxide and ethylene reactions. Some experiments were therefore made to determine the effect of running time on the nitric oxide 'titration' values for active nitrogen from a microwave discharge. It was found (Table 6, Fig. 8) to remain almost unchanged, after prolonged and continuous periods of operation of such a discharge, hence to behave in a manner contrary to that observed for active nitrogen produced in a condensed electrode discharge. The thought then intruded that the slow change in active nitrogen concentration observed with the electrode discharge was probably due to removal of a wall 'poison' during prolonged passage of the active nitrogen through the system (by desorption or reaction, or both), and that a similar change in the nitric oxide 'titration' might be observed with the microwave system if certain wall 'poisons' were present, e.g. water vapour, hydrogen, oxygen. If this were observed, it seemed possible that the presence (or absence, perhaps) of some such wall 'poison' might have been conducive to a NO/HCN ratio of approximately unity during the experiments of Clyne and Thrush.

When water vapour was introduced before the microwave discharge, the active nitrogen was increased (Table 7, Fig. 9) and the afterglow brightened, (visual observation), corresponding to a greater nitrogen atom concentration. Moreover, the 'pink' (Broida) glow was no longer in evidence anywhere in the system. However, the almost immediate return of the system to its normal conditions, when the flow of water vapour was stopped, suggested that the water vapour was dissociated in the discharge region, and probably had little effect as a 'poison' against wall recombination of nitrogen atoms. If water vapour behaved as a wall 'poison', the active nitrogen concentration would probably have changed slowly as adsorbed water was removed from the walls, in the manner observed when a condensed electrode discharge is used. Alternatively, it might even be argued that reversion to the normal 'unpoisoned' behaviour might not have been expected at all, since experiments in the laboratory have shown that active nitrogen from a condensed discharge, but not that from a microwave discharge, will cause decomposition of water. It would appear, then, that the effect of water vapour in altering the active nitrogen concentration in the microwave type of system is due to a change in the extent of dissociation of the nitrogen in the presence of water molecules, or more probably, their dissociation products.

When the water vapour was introduced after the microwave discharge, so that it could act, presumably, only as a wall poison, only a small increase of nitrogen atom concentration occurred. However, the afterglow again brightened, the 'pink' (Broida) glow disappeared, and the system returned immediately to normal conditions when the water vapour supply was stopped. The water molecule apparently reduces the positive ion concentration (a principal component of the 'pink' glow) in the discharged nitrogen.

When nitric oxide was pre-mixed with water vapour, and this mixture was used to titrate active nitrogen, no effect was observed on the nitric oxide 'titration' value (Table 9 and Fig. 11). This suggested that there was no reaction between water vapour and active nitrogen produced in a microwave discharge, an observation which was subsequently confirmed in the laboratory, as indicated above.

The introduction of a trace of hydrogen before the microwave discharge also increased the nitric oxide 'titration' value (Table 10 and Fig. 12), although to an extent somewhat less than that produced by water vapour. Again, the increase might be attributed to a beneficial effect of hydrogen on nitrogen atom production in the discharge. On the other hand, when the flow of hydrogen was stopped, the concentration of active nitrogen dropped to a value that was considerably lower than that attained before the addition of hydrogen. This is rather difficult to explain, but perhaps hydrogen (atomic or molecular) is considerably adsorbed on, or reacts with some component on the walls of the reactor (153), to produce a wall condition that promotes, rather than hinders, loss of nitrogen atoms. When water vapour was passed through the system, for consecutive hourly intervals, the effect induced by the passage of hydrogen was not removed.

The behaviour when traces of oxygen were introduced before the microwave discharge was similar, in many respects, to that observed with hydrogen. This implies, perhaps, that an adsorbed layer was responsible, in both cases, for promoting the loss of nitrogen atoms after the flow of the foreign gas was stopped.

Since there was no effect of operating time, or of traces of additives on the nitric oxide 'titration' value, for active nitrogen produced by a microwave discharge, some study was made of the NO/HCN ratio, at the top and bottom of reactor I. This was done in the knowledge that, with active nitrogen from a condensed discharge, this ratio tends towards unity with decay of the active nitrogen under certain conditions. It was found, however, that the NO/HCN ratio remained almost constant with decay of the active nitrogen in the present system (Table 12, Figs. 14,15), and the addition of traces of water vapour before the microwave discharge had no apparent effect on the ratio. Again, these observations are contrary to the results obtained previously for active nitrogen formed in an electrode discharge (72). For such a system, the NO/HCN ratio decreased, at constant pressure, with time of decay of the active nitrogen in a 'poisoned' system, while in an 'unpoisoned' system the same ratio increased markedly.

It is interesting however, that, in the present experiments, the NO/HCN ratio was found to increase with pressure, to a steady value at a pressure of about 2.5 mm Hg. A similar increase with pressure was reported by Verbeke and Winkler (74). The explanation is probably rather complicated. Increase of pressure may affect several factors that might be involved in the system. For example, an increase in nitrogen atom production in the discharge would be offset by increased rate of gas phase recombination (with N_2 as third body), whereas the rate of diffusion of nitrogen atoms to the wall would be decreased, and wall recombination would be correspondingly less. However, it is also possible that reaction of nitrogen atoms is not limited to the gas phase. In particular, it might be that some hydrogen cyanide is formed at the wall. (It would seem to be less probable that nitric oxide suffers appreciable heterogeneous reaction with nitrogen atoms, since its gas phase reaction is so very fast.) It is also possible that the ethylene reaction involves the intervention of hydrogen atoms (93), as a further complication. With so many factors, and perhaps others, also, that might reasonably be concerned in determining the NO/HCN ratio, it would seem purely conjectural to attempt an explanation for the observed increase in it with increase of pressure.

Since no explanation for the discrepancy between the results of Clyne and Thrush, and those of Mavroyannis and Winkler, was forthcoming from any of the experiments conducted in the reactor I, it was decided that still another approach must be made, and that the oxygen reaction should be re-investigated in a reactor of the type used by Mavroyannis and Winkler.

When this was done, it was found that the maximum oxygen atom production from the active nitrogen-oxygen reaction was in agreement with the maximum hydrogen cyanide production from the active nitrogen-ethylene reaction, i.e. in agreement with the results of Mavroyannis and Winkler (146). This clearly identified the type of reactor as a major determinant of the discrepancy under study, but there remained the necessity for a systematic study of the influence of various features of the reactor to identify the particular factor responsible for the discrepancy.

The introduction of a 300 cc bulb between the discharge tube and the M-W type reactor, such as that used with reactor I, had no effect on the results.

Similarly, elongation of the M-W reactor at the inlet end left unaltered the agreement between the oxygen atom production and the maximum hydrogen cyanide yield from ethylene. However, when the reactor was lengthened at the exit end, the results tended to approach the nitric oxide 'titration' value for the active nitrogen concentration (Table 13). This, coupled with the background information from the previous experiments, provided, at least, a fruitful line of attack in seeking an explanation for the discrepancy between the M-W and C-T experiments. In particular, it compelled re-consideration of the M-W analytical method, when this was used with the M-W, rather than the long-tube type of reactor.

There followed a series of experiments which demonstrated that the satisfactory application of this method for estimating oxygen atom concentrations was, indeed, subject to certain conditions. In particular, the volume available in which reaction might occur, after addition of the excess nitrogen dioxide, was of paramount importance. This might be equally well interpreted, of course, as a requirement for sufficient time in which to allow the reaction to go to completion. Significantly, this reaction volume (or reaction time), following addition of nitrogen dioxide in excess, could be somewhat reduced, apparently, if the mixing efficiency were improved by the use of bulb, instead of tapered, jets.

The conclusion may then be drawn, from the body of data obtained in the present study, that the discrepancy between the results of Mavroyannis and Winkler, and those subsequently obtained by Clyne and Thrush, resides in an unsuspected appreciable time-dependence of the gas-phase formation of N_2O_3 in the analytical method used by Mavroyannis and Winkler. It is true that, according to Mavroyannis (171), the analytical method was checked and found to be satisfactory (within ± 3%), before it was applied to the study of the oxygen reaction. It is not recorded, nor does either of the authors recall*, which jet of the M-W reactor was used to introduce nitrogen dioxide when the analytical method was checked. It is certain, only, that a jet close to the exit of the reactor was used for analytical purposes during the experiments with oxygen. The present investigation leaves no doubt that the location of this jet was such that the reaction time prior to trapping the N_2O_3 was insufficient for the $NO + NO_2$ reaction to achieve completion. The consequence of this would be to make the extent of oxygen atom production from the oxygen reaction

---

*Private communications.

appear to be less than the true value, and bring it into correspondence with the hydrogen cyanide production from ethylene, rather than the nitric oxide 'titration' value.

As a corollary to the above, it must be concluded, finally, that the reaction of atomic nitrogen with molecular oxygen occurs to an extent equal to the nitric oxide 'titration' value for the nitrogen atom concentration in the system, as contended by Clyne and Thrush. This conclusion, in turn, supports this 'titration' value, rather than the maximum hydrogen cyanide yield from ethylene, as a measure of the nitrogen atom concentration in active nitrogen.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The maximum yields of oxygen atoms, from the reactions of active nitrogen with nitric oxide, and with molecular oxygen, respectively, were determined by the nitrogen dioxide 'titration' at various levels in a long-tube reactor, at about 150°C and 2 mm Hg. It was found that the maximum oxygen atom production was essentially the same in both cases.

2. The maximum oxygen atom production from the reaction of active nitrogen with molecular oxygen, in the long-tube reactor, was measured by the excess nitrogen dioxide method, at 400 ± 2°C and 1 and 2 mm Hg. The results again indicated that the maximum oxygen atom concentration was in accordance with the nitric oxide 'titration' value of active nitrogen, and not with the maximum production of hydrogen cyanide from the active nitrogen-ethylene reaction under the same experimental conditions.

3. For the active nitrogen-oxygen reaction,

$$N + O_2 \xrightarrow{k_1} NO + O \; ; \quad \Delta H^\circ = -32.8 \text{ kcal/mole},$$

followed by

$$N + NO \rightarrow N_2 + O \quad ; \quad \Delta H^\circ = -75.1 \text{ kcal/mole},$$

the rate constant k_1 was found to be

$$k_1 = 3.76 \times 10^{12} \exp(-7{,}000/RT) \text{ cc mole}^{-1} \text{ sec}^{-1}$$

over the temperature range 453 to 603^{o}K, and pressure 3 mm Hg.

4. The active nitrogen concentration inferred from the nitric oxide 'titration' remained almost constant, after prolonged and continuous periods of operation of the microwave discharge, at the pressures of 2, 3 and 4 mm Hg.

5. The effects of certain additives, such as water vapour, hydrogen and oxygen, on the nitric oxide 'titration' value of active nitrogen were studied. All of them showed, more or less, a common behaviour when introduced before the microwave discharge. This, combined with other observations, suggested that these substances, or their dissociation products in the discharge, promoted the dissociation of nitrogen.

6. It was found that the NO/HCN ratio remained almost unchanged near the inlet, and near the exit of the reactor, whether in an 'unpoisoned' or a 'poisoned' system, i.e. it remained constant with decay of active nitrogen, at constant pressure and room temperature. However, the same ratio increased with pressure, over the range of pressures from 0.75 to 2.5 mm Hg, and finally reached a plateau value at 2.5 mm Hg, and remained constant with further increase of pressure to 3, 4 and 5 mm Hg.

7. The maximum oxygen atom production from the reaction of active nitrogen with molecular oxygen, in a short reactor with multiple jets (such as that used by Mavroyannis and Winkler), was in agreement with the maximum yield of hydrogen

cyanide from the active nitrogen-ethylene reaction. This deviation from the previous results was finally traced to a deficiency in the analytical method based on the trapping N_2O_3 in the presence of excess nitrogen dioxide.

8. This analytical method was reliable only if sufficient volume was available (i.e. sufficient reaction time was permitted), after the inlet point for nitrogen dioxide, to permit the NO + NO_2 reaction to go to completion. The deficiency of the analytical method provided an answer to the discrepancy between the earlier studies by Clyne and Thrush, on one hand, and those of Mavroyannis and Winkler on the other.

9. For the reaction of nitric oxide with nitrogen dioxide,

$$NO + NO_2 \xrightarrow{k} N_2O_3$$

the rate constant k was estimated to be

$$k = 1.3 \times 10^{9} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

at 30°C, and pressure 3.3 mm Hg.

BIBLIOGRAPHY

1. Warburg, E., Arch. de Gen., (3) 12, 504 (1884).
2. Lewis, P.E., Astrophys. J., 12, 8 (1900).
3. Strutt, R.J., Proc. Roy. Soc. (London), A85, 219 (1911).
   Ibid. A86, 56 (1912).
   Ibid. A88, 539 (1913).
   Ibid. A91, 303 (1915).
4. Mitra, S.K., 'Active Nitrogen - A New Theory', Association for the Cultivation of Science, Calcutta, India (1945).
5. Jennings, K.R. and Linnett, J.W., Quart. Rev., 12, 116 (1958).
6. Edwards, J.W., 'Formation and Trapping of Free Radicals', edited by Bass, A.M. and Broida, H.P., Academic Press, New York (1960).
7. Manella, G.G., Chem. Rev., 63, 1 (1963).
8. Burke, J.B.B., Phil. Mag., 1, 342 (1901).
9. Stanley, C.R., Proc. Phys. Soc., A67, 821 (1954).
10. Armstrong, D.A. and Winkler, C.A., J. Phys. Chem., 60, 1100(1956).
11. Kenty, C. and Turner, L.A., Phys. Rev., 32, 799 (1928).
12. Comte, F.A., Z. Physik, 14, 74 (1913).
13. Lewis, B., J. Am. Chem. Soc., 51, 654 (1929).
14. Rayleigh, Lord, Proc. Roy. Soc. (London), A151, 567 (1935).
15. Anderson, J.M., Proc. Phys. Soc., A70, 887 (1957).
16. Bonhoeffer, K.F. and Kaminsky, G., Z. Phys. Chem., 127, 385 (1927).
17. Rayleigh, Lord, Proc. Roy. Soc. (London), A180, 140 (1942).
18. Benson, J.M., J. Appl. Phys., 23, 757 (1952).
19. Willey, E.J.B. and Rideal, E.K., J. Chem. Soc., 669 (1927).

20. Rayleigh, Lord, Proc. Roy. Soc. (London), A102, 453 (1922).

21. Kaplan, J., Nature, 122, 771 (1928).

22. McLennan, J.C., Ruedy, R., and Anderson, J.W., Trans. Roy. Soc. Can., 22, 303 (1928).

23. Kaplan, J., Phys. Rev., 33, 189 (1929).

24. Reinecke, L.H., Z. Physik, 135, 361 (1953).

25. Herzberg, G.H., Z. Physik, 46, 878 (1928).

26. Kistiakowsky, G.B. and Warneck, P., J. Chem. Phys., 27, 1417 (1957).

27. Berkowitz, J., Chupka, W.A., and Kistiakowsky, G.B., J. Chem. Phys., 25, 457 (1956).

28. Rayleigh, Lord, Proc. Roy. Soc. (London), A176, 1 (1940).

29. Willey, E.J.B. and Rideal, E.K., J. Chem. Soc., 1804 (1926).

30. Okubo, J. and Hamada, H., Phil. Mag., 5, 372 (1928).

31. Foote, P.D., Ruark, A.E., and Chenault, R.L., Phys. Rev., 25, 241 (1925).

32. Rayleigh, Lord, Proc. Roy. Soc. (London), A176, 16 (1940).

33. Herzberg, G., 'Molecular Spectra and Molecular Structure. I. Diatomic Molecules', Van Nostrand, New York (1950). p. 450.

34. Gaydon, A.G., Nature, 153, 407 (1944).

35. Gaydon, A.G., 'Dissociation Energies and Spectra of Diatomic Molecules', Chapman and Hall, London (1953). pp. 152-162.

36. Kistiakowsky, G.B., Knight, H.T., and Malin, M.E., J. Am. Chem. Soc., 73, 2972 (1951).

37. Hendrie, J.M., J. Chem. Phys., 22, 1503 (1954).

38. Frost, D.C. and McDowell, C.A., Proc. Roy. Soc. (London), A236, 278 (1956).

39. Wood, R.W., Phil. Mag., 44, 538 (1922).

40. Bonhoeffer, K.F., Z. Physik. Chem., 113, 199 (1924).

41. Sponer, H., Z. Physik, 34, 622 (1925).

42. Cario, G. and Kaplan, J., Z. Physik, 58, 769 (1929).
Nature, 121, 906 (1928).

43. Jackson, L.C. and Broadway, L.F., Proc. Roy. Soc. (London), A127, 678 (1930).

44. Worley, R.E., Phys. Rev., 73, 531 (1948).

45. Herbert, W.S., Herzberg, G., and Mills, G.A., Can. J. Res., A15, 35 (1937).

46. Cario, G., Z. Physik, 89, 523 (1934).

47. Mitra, S.K., Phys. Rev., 90, 516 (1953).

48. Brook, M., Phys. Rev., 92, 1079 (1953).

49. Peyron, M. and Broida, H.P., J. Physique, 18, 593 (1957).

50. Le Blanc, F., Tanaka, Y., and Jursa, A., J. Chem. Phys., 28, 979 (1958).

51. Bayes, K.D. and Kistiakowsky, G.B., J. Chem. Phys., 32, 992 (1960).

52. Dunford, H.B., J. Phys. Chem., 67, 258 (1963).

53. Wrede, E.P., Z. Physik, 54, 53 (1929).

54. Tanaka, N., Jursa, A., and Le Blanc, F., 'The Threshold of Space', edited by Zelikoff, M., Pergamon Press, New York (1960). p. 89.

55. Bass, A.M. and Broida, H.P., Phys. Rev., 101, 1740 (1956).

56. Peyron, M. and Broida, H.P., J. Chem. Phys., 30, 139 (1959).

57. Heald, M.A. and Beringer, R., Phys. Rev., 96, 645 (1954).

58. Jackson, D.S. and Schiff, H.I., J. Chem. Phys., 23, 2333 (1955).

59. Herzberg, G., 'Atomic Spectra and Atomic Structure', Dover Publications (1944). p. 200.

60. Thrush, B.A., Proc. Roy. Soc. (London), A235, 143 (1956).

61. Milligan, D.E., Brown, H.W., and Pimentel, G.J., J. Chem. Phys., 25, 1080 (1956).

62. Harvey, K.B. and Brown, H.W., J. Chim. Phys., 56, 745 (1959).

63. Evans, H.G.V. and Winkler, C.A., Can. J. Chem., 34, 1217 (19

64. Kaufman, F. and Kelso, J.R., J. Chem. Phys., 28, 510 (1958).

65. Lipscomb, F.J., Norrish, R.G.W., and Thrush, B.A., Proc. Roy. Soc. (London), A233, 455 (1956).

66. Dressler, K., J. Chem. Phys., 30, 1621 (1959).

67. Morgan, J.E. and Schiff, H.I., Can. J. Chem., 41, 903 (1963)

68. Starr, W.L., J. Chem. Phys., 43, 73 (1965).

69. Starr, W.L. and Shaw, T.M., J. Chem. Phys., 44, 4181 (1966).

70. Morgan, J.E., Phillips, L.F., and Schiff, H.I., Disc. Faraday Soc., 33, 118 (1962).

71. Freeman, G.R. and Winkler, C.A., J. Phys. Chem., 59, 371 (1959).

72. Wright, A.N., Nelson, R.L., and Winkler, C.A., Can. J. Chem., 40, 1082 (1962).

73. Kistiakowsky, G.B. and Volpi, G.G., J. Chem. Phys., 28, 665 (1958).

74. Verbeke, G.J. and Winkler, C.A., J. Phys. Chem., 64, 319 (196

75. Khawaja, N.A., Ph.D. Thesis, McGill University (1962).

76. Jones, W.E. and Winkler, C.A., Can. J. Chem., 42, 1948 (1964).

77. Freeman, C.G. and Phillips, L.F., J. Phys. Chem., 68, 362 (1964).

78. Lichten, W., J. Chem. Phys., 26, 306 (1957).

79. Wilkinson, P.G. and Mulliken, R.S., J. Chem. Phys., 31, 674 (1959).

80. Noxon, J.F., J. Chem. Phys., 36, 926 (1962).

81. Carleton, N.P. and Oldenberg, O., J. Chem. Phys., 36, 3460 (1962).

82. Zipf, E.C., J. Chem. Phys., 38, 2034 (1963).

83. Phillips, L.F., Can. J. Chem., 43, 369 (1965).

84. Young, R.A., Can. J. Chem., 44, 1171 (1966).

85. Paraskevopoulos, G., Ph.D. Thesis, McGill University (1965).

86. Kistiakowsky, G.B. and Volpi, G.G., J. Chem. Phys., 27, 1141 (1957).

87. Clyne, M.A.A. and Thrush, B.A., Proc. Roy. Soc. (London), A261, 259 (1961).

88. Kaufman, F. and Kelso, J.R., J. Chem. Phys., 27, 1209 (1957).

89. Back, R.A. and Mui, J.U.P., J. Phys. Chem., 66, 1362 (1962).

90. Zinman, N.G., J. Phys. Chem., 64, 1343 (1960).

91. Fersht, E. and Back, R.A., Can. J. Chem., 43, 1899 (1965).

92. Dubrin, J., MacKay, C., and Wolfgang, R., J. Chem. Phys., 44, 2208 (1966).

93. Herron, J.T., J. Phys. Chem., 69, 2736 (1965).

94. Westenberg, A.A. and De Haas, N., J. Chem. Phys., 40, 3087 (1964).

95. Von Weyssenhoff, H. and Patapoff, M., J. Phys. Chem., 69, 1756 (1965).

96. Morse, F.A. and Kaufman, F., J. Chem. Phys., 42, 1785 (1965).

97. Elias, L., J. Chem. Phys., 44, 3810 (1966).
Ibid. 42, 4311 (1965).

98. Spealman, M.L. and Rodebush, W.H., J. Am. Chem. Soc., 57, 1474 (1935).

99. Lewis, B., J. Am. Chem. Soc., 50, 27 (1928).

100. Evans, H.G.V., Freeman, G.R., and Winkler, C.A., Can. J. Chem., 34, 1271 (1956).

101. Greenblatt, J.H. and Winkler, C.A., Can. J. Res., B27, 721 (1949).

102. Versteeg, J. and Winkler, C.A., Can. J. Chem., 31, 1 (1953).

103. Herron, J.T., Franklin, J.L., and Bradt, P., Can. J. Chem., 37, 579 (1959).

104. Mavroyannis, C. and Winkler, C.A., Can. J. Chem., 40, 240 (1962).

105. Trick, G.S. and Winkler, C.A., Can. J. Chem., 30, 915 (1952).

106. Shinozaki, Y., Shaw, R., and Lichtin, N.L., J. Am. Chem. Soc., 86, 341 (1964).

107. Gesser, H., Luner, C., and Winkler, C.A., Can. J. Chem., 31, 346 (1953).

108. Versteeg, J. and Winkler, C.A., Can. J. Chem., 31, 129 (1953)

109. Shavo, A. and Winkler, C.A., Can. J. Chem., 37, 655 (1959).

110. Wright, A.N. and Winkler, C.A., Can. J. Chem., 40, 1291 (1963).

111. Gartaganis, P.A. and Winkler, C.A., Can. J. Chem., 34, 1457 (1956).

112. Blades, H. and Winkler, C.A., Can. J. Chem., 29, 1022 (1951).

113. Onyszchuk, M., Breitman, L., and Winkler, C.A., Can. J. Chem., 32, 351 (1954).

114. Back, R.A. and Winkler, C.A., Can. J. Chem., 32, 718 (1954).

115. Onyszchuk, M. and Winkler, C.A., J. Phys. Chem., 59, 368 (1955).

116. Klassen, N.V., Onyszchuk, M., McCabe, J.C., and Winkler, C.A., Can. J. Chem., 36, 1217 (1958).

117. Armstrong, D.A. and Winkler, C.A., Can. J. Chem., 33, 1649 (1955).

118. Dunford, B., Evans, H.G.V., and Winkler, C.A., Can. J. Chem., 34, 1074 (1956).

119. Freeman, G.R. and Winkler, C.A., J. Phys. Chem., 59, 780 (1955).

120. Forst, W. and Winkler, C.A., J. Phys. Chem., 60, 1424 (1956).

121. Armstrong, D.A. and Winkler, C.A., Can. J. Chem., 34, 885 (1956).

122. Sole, M.J. and Gartaganis, P.A., Can. J. Chem., 41, 1097 (1963).

123. Gartaganis, P.A., Can. J. Chem., 43, 935 (1965).

124. Haggart, C. and Winkler, C.A., Can. J. Chem., 38, 329 (1960).

125. Rabinowitch, E., Trans. Faraday Soc., 33, 283 (1937).

126. Harteck, P., Reeves, R.R., and Mannella, G., J. Chem. Phys., 29, 608 (1958).

127. Herron, J.T., Franklin, J.L., Bradt, P., and Dibeler, V.H., J. Chem. Phys., 30, 879 (1959).

128. Wentink, T., Sullivan, J.D., and Wray, K.L., J. Chem. Phys., 29, 231 (1958).

129. Mavroyannis, C. and Winkler, C.A., Can. J. Chem., 39, 1601 (1961).

130. Clyne, M.A.A. and Thrush, B.A., Trans. Faraday Soc., 57, 69 (1961).

131. Phillips, L.F. and Schiff, H.I., J. Chem. Phys., 42, 3171 (1965).

132. Zabolotny, E.R. and Gesser, H., J. Chem. Phys., 36, 565 (1962).

133. Milton, E.R.V., Dunford, H.B., and Douglas, A.E., J. Chem. Phys., 35, 1202 (1961).

134. Wiles, D.M. and Winkler, C.A., Can. J. Chem., 35, 1298 (1957).

135. Milton, E.R.V. and Dunford, H.B., J. Chem. Phys., 34, 51 (1961).

136. Khanna, S.N. and Winkler, C.A. To be published.

137. Wiles, D.M. and Winkler, C.A., J. Phys. Chem., 61, 902 (1957).

138. Vadlamudy, S.V. and Winkler, C.A. To be published.

139. Brennen, W.R. and Kistiakowsky, G.B., J. Chem. Phys., 44, 2695 (1966).

140. Westbury, R.A. and Winkler, C.A., Can. J. Chem., 38, 334 (1960).

141. Jacob, A., Westbury, R.A. (Mrs.), and Winkler, C.A. To be published in J. Phys. Chem.

142. Smith, J.J. and Jolly, W.L., Inorg. Chem., 4, 1006 (1965).

143. Bett, J.A.S. and Winkler, C.A., J. Phys. Chem., 68,2501 (1964).

144. Varney, R.N., J. Chem. Phys., 23, 866 (1955).

145. Kaufman, F. and Decker, L.J., Seventh Symp. 'Combustion Institute' p. 57 (Sept. 1958).

146. Mavroyannis, C. and Winkler, C.A., International Symposium on the Chemistry of the Lower and Upper Atmosphere, San Francisco, Calif., p. 177 (April 1961).

147. Willey, E.J.B., J. Chem. Soc,, 1146 (1930).

148. Willey, E.J.B., J. Chem. Soc., 336 (1930).

149. Kaplan, J., Nature, 136, 549 (1935).

150. Rayleigh, Lord, Proc. Roy. Soc. (London), A180, 123 (1942).

151. Young, R.A., Sharpless, R.L., and Stringham, R., J. Chem. Phys., 40, 117 (1964).

152. Herron, J.T., J. Res. Natl. Bur. Std., A69, 287 (1965).

153. Anderson, J.M., Proc. Phys. Soc., 87, 299 (1966).

154. McCormick, K.S. and Anderson, J.M., Proc. Phys. Soc., 87, 311 (1966).

155. Back, R.A. and Winkler, C.A. Unpublished Results.

156. Storr, R., Wright, A.N., and Winkler, C.A., Can. J. Chem., 40, 1296 (1962).

157. Verhoek, F.H. and Daniels, F., J. Am. Chem. Soc., 53, 1250 (1931).

158. Kolthoff, I.M. and Sandell, E.B., 'Textbook of Quantitative Analysis', McMillan Co., New York (1952).

159. Kaufman, F., Proc. Roy. Soc. (London), A247, 123 (1958).
J. Chem. Phys., 28, 352 (1958).

160. Morgan, J.E., Ph.D. Thesis, McGill University (1962).

161. Sobering, S.E. and Winkler, C.A., Can. J. Chem., 36, 1223 (1958).

162. Beattie, I.R., Progr. Inorg. Chem. (F.A. Cotton, editor. Interscience), 5, 1 (1963).

163. Abel, E. and Proisl, J., Z. Elektrochem., 35, 712 (1929).

164. Beattie, I.R. and Bell, S.W., J. Chem. Soc., 1681 (1957).

165. Hisatsune, I.C. and Devlin, J.P., Spectrochim. Acta, 16, 401 (1960).

166. Ashmore, P.G. and Tyler, B.J., J. Chem. Soc., 1017 (1961).

167. Leifer, E., J. Chem. Phys., 8, 301 (1940).

168. Benson, S.W., 'The Foundations of Chemical Kinetics', McGraw-Hill Co., New York (1960). p. 81.

169. Ashmore, P.G. and Levitt, B.P., Research, 9, S25 (1956).

170. Ashmore, P.G. and Burnett, M.G., Trans. Faraday Soc., 58, 253 (1962).

171. Mavroyannis, C., Ph.D. Thesis, McGill University (1961). p. 77