A. Jacob

THE REACTIONS OF ACTIVE NITROGEN WITH OXIDES OF SULPHUR

ABSTRACT

Practically no decomposition of NH_3 and SO_2 was observed with a "poisoned" microwave discharge system, while a "poisoned" condensed discharge, of comparable N atom concentration, induced distinct consumption of these gases. The very similar relative behaviour of NH_3 and SO_2 in their reactions with active nitrogen, and their comparable effects on some active nitrogen - hydrocarbon reactions, suggest that $N_2(A^3\Sigma_u^+)$ is probably the species responsible for energy transfer to NH_3 and SO_2 to effect their decomposition.

The stable products of the SO_2 decomposition are SO_3 and sulphur-nitride (S_4N_4, S_2N_2 and $(SN)x$), probably due to O and S atoms derived from the transient SO molecule. The amount of SO_2 destroyed was found to decrease with increase in SO_2 flow rate. This was ascribed to deactivation of the excited $SO_2{}^*$ by SO_2 itself, in competition with destruction of $SO_2{}^*$ by nitrogen atoms and its spontaneous decomposition to SO + O. The initial energy exchange between N_2 $(A^3\Sigma_u^+)$ and SO_2 was estimated to have a rate constant 7×10^{-15} cc/molec-sec at 333^oK. The overall activation energy for destruction of SO_2 by active nitrogen was about 2 kcal/mole in the range 333 to 688^oK.

The reactions of SO and SO_3 with nitrogen atoms yield NO and SO_2, respectively, and are associated with rate constants of 1.5×10^{-12} and 5.4×10^{-16} cc/molec-sec, respectively at 300^oK and at 2 torr pressure. The SO_3 reaction was found to have an overall activation energy of about 2.3 kcal/mole in the range 300 to 523^oK.

TITLE:

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THE REACTIONS OF ACTIVE NITROGEN WITH OXIDES OF SULPHUR

by

Adir Jacob

B.Sc. (Jerusalem)

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.

April, 1968.

TO MY WIFE
ROLLY

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INTRODUCTION

Since the discovery by Lewis (1) of the persistent golden-yellow afterglow in nitrogen subjected to an electrical discharge, the phenomenon has been the subject of many investigations to establish the nature of the species generated by the discharge. Strutt (later, Lord Rayleigh) (2) initiated a comprehensive study of the physical and chemical properties of the glowing gas, and showed that it had great chemical reactivity. Accordingly, he gave to it the now familiar name of "active nitrogen", and it is interesting to note that he associated the activity with the presence of nitrogen atoms. Since then, in numerous investigations of the spectra of the afterglow, and the physical and chemical properties of active nitrogen, the data have been and still are replete with disagreements and contradictions. These are due partly, perhaps, to the complex nature of active nitrogen, and partly to technical problems that may be encountered during studies of the highly reactive system that is involved.

Most of the investigations that have been made at relatively low pressures (a few torr) have led to the conclusion that the energetic components of active nitrogen may include not only ground state, $N(^4S)$, atoms (3), and vibrationally excited ground state nitrogen molecules (4), but also, under suitable conditions, significant concentrations of electronically excited nitrogen molecules, e.g., $A^3\Sigma_u^+$ (5). Metastable nitrogen atoms (^2D, ^2P) have been observed by absorption spectroscopy (3), but in concentrations about three orders of magnitude lower than that of the ground state atoms.

It is likely that the metastable atoms and molecules are produced mainly in the discharge itself, rather than subsequently, and that their production is largely a function of the electrical discharge parameters.

The complex behaviour of active nitrogen is not only a function of the many possible interactions of its several components, but is also markedly influenced by the purity of the gas and by surface conditions in the system. As a consequence, different experimental conditions may lead to apparently conflicting observations. Nevertheless, there is now a considerable measure of agreement about the rates and mechanisms of some of simpler reactions of active nitrogen, e.g., with atoms and diatomic and triatomic molecules. Reactions with larger molecules, such as hydrocarbons and hydrocarbon derivatives are yet relatively little understood.

The literature on active nitrogen has been summarized a number of times (6,7,8,9,32). The review that follows will, therefore, make no attempt to be comprehensive. Rather, the intention will be to outline those aspects of the subject that are directly relevant to discussion of the results of the present investigation.

THE NITROGEN AFTERGLOW

Production of the afterglow

Excitation of nitrogen to produce the characteristic yellow afterglow (known as the Lewis-Rayleigh glow) may be achieved in a number of ways, some of which are classical, e.g., condensed dc discharge, uncondensed ac discharge, high frequency electrodless discharge, electron bombardment, while others are of more recent development, e.g., shock tube techniques (10), exposure to radio active sources (11), and discharge through NO or NH_3 (12). The intensity of the glowing gas is dependent on the conditions of the experiment; it can be quite high and can be observed at a relatively large distance from the means of excitation, if the reaction vessel is suitably conditioned to prevent decay of the active nitrogen on the wall. It is well established that the afterglow in pure N_2 is very much weaker than that obtained by nitrogen to which traces of impurities such as O_2, H_2O or H_2 are added before it enters the discharge tube. As early as 1911, Strutt (2) observed that certain gases brightened the yellow afterglow considerably when they were added to a nitrogen discharge. The effect was also observed if the gases were added after the discharge, and qualitative observations enabled him to place their effectiveness in the order, $H_2S>H_2O>CO_2>C_2H_2>C_2H_6>CH_4>O_2>Hg>Cl_2>H_2>Ar>He>N_2$. In a later study (13), he followed the change in the intensity of the nitrogen afterglow as a function of measured amounts of added oxygen to the discharge, and concluded that oxygen enhanced the glow.

In a similar study of the rate of decay of the afterglow in the presence of different gases, Willey (14) concluded that the surface catalyzed recombination of nitrogen atoms decreased with increasing impurity content, while a concomitant increase in the homogeneous recombination occurred, up to a limit of about 0.1% of impurity present. When this limit was exceeded, the production of the afterglow was inhibited, since nitrogen atoms were then, presumably, removed by chemical reaction.

Lewis (15) also observed a marked effect of water vapour on the production of the afterglow. On the other hand, Kaplan (16) was unable to obtain the afterglow in the presence of a trace of hydrogen.

More recently, it has been observed that the addition of NO, O_2, or SF_6, either before or after the discharge, resulted in an increase of the nitrogen atom concentration (17). These observations have been confirmed by mass spectrometric studies of the effects of NO, O_2, NH_3, and SF_6 on "purified" active nitrogen (18). The addition of these gases in various proportions, before a microwave discharge, resulted in a threefold increase in the partial pressure of the nitrogen atoms, while their addition after the discharge resulted in a twofold increase (except with SF_6, which then had little effect).

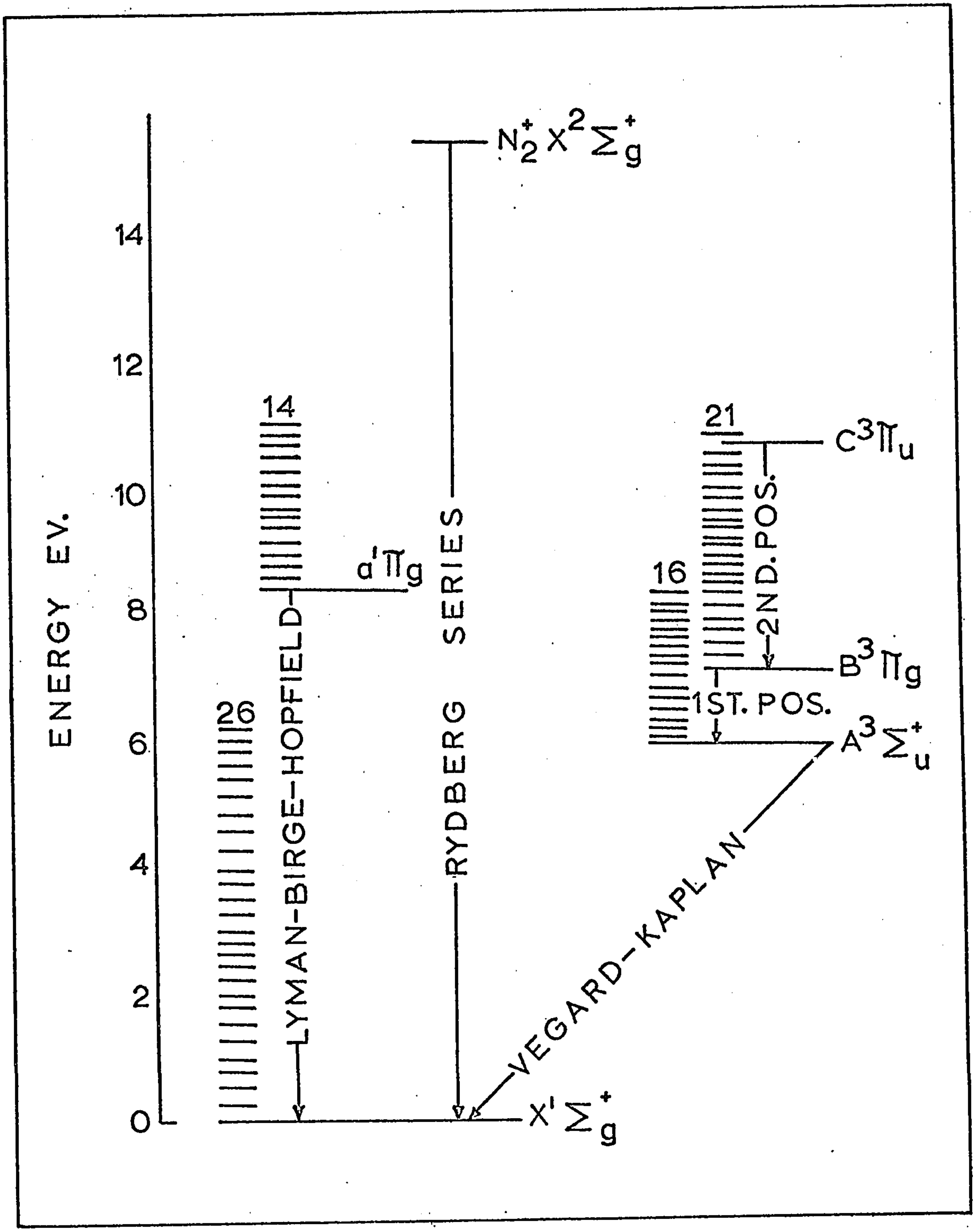
The effect of these impurities is not thoroughly understood. It is not unlikely, however, that their presence might affect the production of nitrogen atoms in the discharge by affecting the recombination of atoms, homogeneously or heterogeneously, in the discharge tube, or perhaps by altering the mechanism of the discharge process itself.

Energy and energy states of nitrogen

The emission spectra of the Lewis-Rayleigh afterglow consists of selected bands of the First Positive System of the N_2 molecule (Fig. 1). These bands are due to a transition from the higher $N_2(B^3\Pi_g)$ state to the lower $N_2(A^3\Sigma_u^+)$ state from which the molecules reach the ground state, $N_2(X^1\Sigma_g^+)$, by losing their excess energy by collisional deactivation. From spectral analysis of the First Positive System, it appears that these bands are due to transitions from the twelfth, eleventh, tenth and sixth vibrational levels of the B state. Transitions from

Figure 1

Energy levels of molecular nitrogen. The long and short horizontal lines indicate the electronic states and the vibrational levels, respectively. (Reproduced from ref. 24)


ENERGY EV.
0
2
4
6
8
10
12
14
$N_2^+ X^2\Sigma_g^+$
14
21
$C^3\Pi_u$
$a'\Pi_g$
16
2ND. POS.
$B^3\Pi_g$
26
LYMAN-BIRGE-HOPFIELD
RYDBERG SERIES
1ST. POS.
$A^3\Sigma_u^+$
VEGARD-KAPLAN
$X'\Sigma_g^+$

V=13 or higher are never observed. Bands of NO, in the blue and U.V. regions of the spectrum, are usually also present in the afterglow, the intensity of which is proportional to the amount of oxygen impurity in the system. The First Positive emission spectrum is quite different from that of the discharge itself, which consists of the Second Positive System of N_2, corresponding to the transition $(C^3\Pi_u \rightarrow B^3\Pi_g)$ (Fig. 1).

The energy content of active nitrogen has been estimated by various investigators. Strutt (19) observed a temperature rise of a copper oxide probe when active nitrogen was destroyed on it. However, the temperature of the probe was not changed when NO was added to the active nitrogen before it reached the probe. He concluded that active nitrogen did not contain a high amount of energy.

An energy content of about 2 eV/mole of total nitrogen was suggested by Willey and Rideal (20) on the basis of calorimetric methods. Since active nitrogen was incapable of reacting with H_2, HCl, or N_2O, all with dissociation energies of over 60kcal/mole, they concluded that active nitrogen lacks the energy necessary for reaction with these substances. On the other hand, excitation of band spectra in the ultraviolet led Knauss (21) to suggest the presence of metastable molecules in active nitrogen with 9 to 10 eV excess energy. Lord Rayleigh, in a later experiment (22), inferred a value as high as 12.9 eV/mole of total nitrogen from the temperature attained by a metal foil which was exposed to an active nitrogen stream. It has since been shown by Benson (23) that a greater part of this heating effect was due to electron bombardment from the discharge.

A quantity closely related to the energy content of active nitrogen is the bond dissociation energy of the ground state N_2 molecule, the value of which was controversial until quite recently. The values proposed were 7.373 and 9.764 eV. The first was suggested by Herzberg (24) on the basis of predissociations observed in the $N_2(C^3\Pi_u)$ and $N_2(B^3\Pi_g)$ states. The corresponding dissociation products, $N(^2D) + N(^2D)$ and $N(^4S) + N(^2D)$, at these prodissociation limits, yielded the upper limiting values of 7.377 and 7.46 eV for $D(N_2)$. Gaydon (25), on the other hand, attributed the predissociation in the $B^3\Pi_g$ state of nitrogen to the recombination of ground state nitrogen atoms through the loosely-bound $^5\Sigma_g^+$ state of N_2, which led to a dissociation energy of 9.764 eV. More recently, studies on the thermal decomposition of nitrogen (26), and the dissociation of N_2 by monoenergetic electron impact (27), provided strong support for the higher value and 9.756 eV/mole (225 kcal/mole) is now accepted for $D(N_2)$.

The emission spectra of active nitrogen in the Lewis-Rayleigh region, or of substances added to it, are associated mainly with excitation energies below the dissociation energy of N_2 (9.76 eV). This supports the view that the $N(^4S)$ atom recombination may be the main source of energy in the glowing gas. Apart from spectroscopic studies that indicated the presence of other species in the afterglow, chemical studies (e.g., with NH_3, I_2) have led to the suggestion that active nitrogen contains energetic species, other than N atoms, which can participate in chemical reactions. Some relevant electronically excited states of nitrogen below its dissociation limit are given below, along with their lowest energy content.

State:	$A^3\Sigma_u^+$	$B^3\Pi_g$	$^3\Delta_u$	$a^1\Pi_g$	$^5\Sigma_g^+$
energy (eV):	6.17	7.35	7.5	8.64	9.66

<u>Mechanism of the Lewis-Rayleigh afterglow</u>

Since the discovery of active nitrogen, several mechanisms have been proposed for the release of energy that it represents. Many of the earlier studies, however, were hindered by uncertainties about the dissociation energy of N_2 and by failure to recognize the effect of purity of the nitrogen and the condition of the walls of the reaction system.

On the basis of Rayleigh's suggestion (2) that active nitrogen contained nitrogen atoms, Sponer (28) proposed the earliest theory of the afterglow based on a two-step mechanism:

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

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

This rare triple collision in the gas phase (at low pressures) could explain the observed long persistence and the decay process of the afterglow. Now that the bond dissociation energy of N_2 is known to be 9.76 eV, this theory can also support all the valid observations on the energy associated with active nitrogen. However, the mechanism fails to explain the selective enhancement of certain vibrational bands in the spectrum of the glowing gas.

A theory advanced by Cario and Kaplan (29) assumed that active nitrogen is a mixture of metastable atoms and molecules, which gave rise to the afterglow by

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

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

Since this mechanism was able to explain the selective enhancement of the First Positive System (the B state would then be formed in the twelfth vibrational level), it was preferred to the atomic formulation of Sponer. However, as stated above, no evidence of $N(^2P)$ in concentrations appropriate to this process has ever been detected. Similarly, it was also thought that the $N_2(A^3\Sigma_u^+)$

state might be too short lived for such an encounter, but more recent studies (30,31) indicated that this is not a valid objection.

The existence of charged particles in active nitrogen, which was inferred from Rayleigh's metal-foil experiments, led Mitra (32) in 1945 to suggest that active nitrogen consisted primarily of a mixture of N_2^+ ions and electrons, which would readily explain both the conductivity and the mechanism of the afterglow. He proposed the mechanism

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

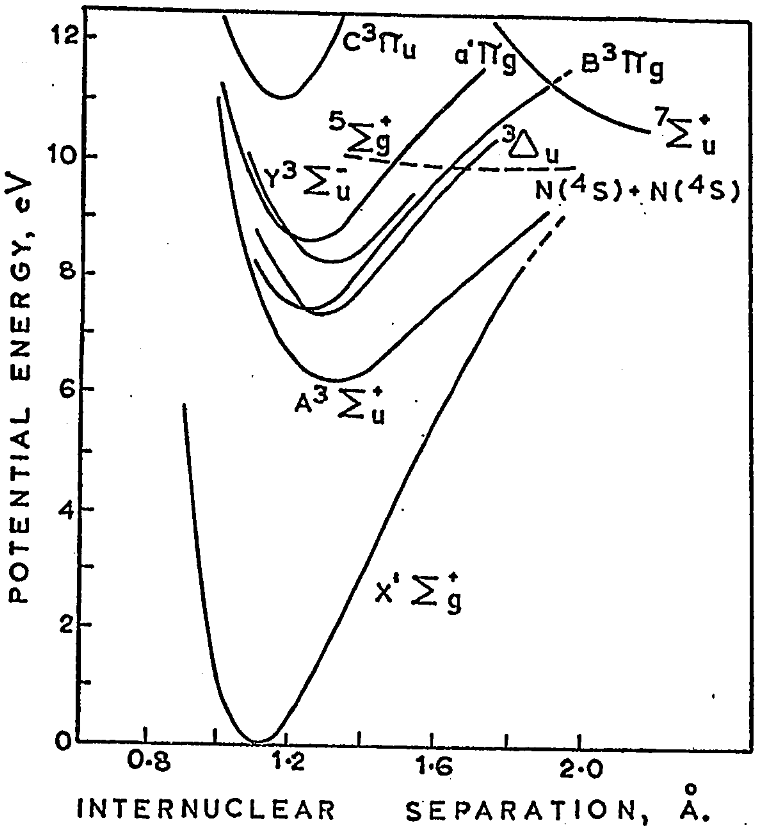
This theory also explained the long life time of the glow. However, Benson (23) later repeated Rayleigh's metal-foil experiment in a modified apparatus, but was not able to reproduce Rayleigh's results. He also showed that the intensity of the afterglow was unaffected by removal of charged particles and by a magnetic field. The conductive nature of the gas then was ascribed to a low concentration of electrons compared with the total concentration of the active particles. The electron-ion mechanism was therefore rejected.

An atomic recombination mechanism is now the generally accepted theory of the afterglow. Although two $N(^4S)$ atoms can approach each other along any one of four potential energy curves, the $X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$, the approach by the $^5\Sigma_g^+$ potential curve was suggested by Gaydon (25) as the most likely to produce the emission cascade. He postulated that the potential energy curve of this weakly-bound molecule, evidence for which was obtained by work on active nitrogen at very low temperatures (33), crossed that of the B state (Fig. 2) thus explaining the predissociation observed in the First Positive System of nitrogen. He argued that molecules of the B state in vibrational levels V=13-16 may undergo a collision-induced radiationless transition to extremely low vibrational levels of the $^5\Sigma_g^+$ state, which would ultimately dissociate into ground state nitrogen atoms. It is then clear that the reverse of this predissociation enables ground state nitrogen atoms, $N(^4S)$, to produce molecules in the B state. This is possible if, in the afterglow, two ^4S atoms approach each other along the $^5\Sigma_g^+$ potential curve, after which pre-association into the twelfth vibrational level of the B state is induced by a third body.

Kistiakowsky and Warneck (34) supported Gaydon's view by suggesting the mechanism

Figure 2

Potential energy curves for the nitrogen molecule
(Reproduced from refs. 8, 38)


$C^3\Pi_u$
$a^1\Pi_g$
$B^3\Pi_g$
$^5\Sigma_g^+$
$^7\Sigma_u^+$
$^3\Delta_u$
$Y^3\Sigma_u^-$
$N(^4S) + N(^4S)$
$A^3\Sigma_u^+$
$X^1\Sigma_g^+$
12
10
8
6
4
2
0
0·8
1·2
1·6
2·0
POTENTIAL ENERGY, eV
INTERNUCLEAR SEPARATION, Å.

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

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

They concluded however, that it applied only to vibrational levels, V=8-12 of the B state, while lower vibrational levels appeared to be populated by a new state, "Y". This new state is formed from the $^5\Sigma_g^+$ state molecules by a radiationless, collision-induced transition in competition with the process forming the $B^3\Pi_g$ state.

The observation of the Lyman-Birge-Hopfield bands in the afterglow (35) corresponding to the transition $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ (Fig. 1) can be explained in the same way. Gaydon (36) suggested that two ^4S atoms collide on the $^5\Sigma_g^+$ potential energy curve, after which a collision with a third body induces a predissociation into the sixth vibrational level of the $a^1\Pi_g$ state, also in competition with the process forming the previously mentioned B and Y states.

The $^3\Delta_u$ state of nitrogen was postulated by Le Blank *et al* (37) as the upper state of a new band system. Predissociation data for this state also support its formation by a collision-induced radiationless transition from the $^5\Sigma_g^+$ state (Fig. 2).

A rather detailed mechanism for the Lewis-Rayleigh afterglow has been proposed by Bayes and Kistiakowsky (38). The data are based upon the relative intensities in the nitrogen afterglow, from 5000 to 11000 Å, in pure nitrogen and after addition of several foreign gases. The mechanism attempts to account for most of the afterglow emission and can be summarized as follows:

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

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

(First Positive System)

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

(Proposed new bands)

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

(Proposed new bands)

$$\longrightarrow N_2(a^1\Pi_g) \longrightarrow N_2(X^1\Sigma_g^+) + h\nu$$

(Lyman-Birge-Hopfield bands)

The observed group bands may sometimes be accompanied by the transition,

$$N_2(A^3\Sigma_u^+) \longrightarrow N_2(X^1\Sigma_g^+) + h\nu$$

This corresponds to the vegard-Kaplan emission, which is observed in very pure nitrogen and is usually enhanced in the presence of argon (33). The above mechanism accounts reasonably well for the major features of the nitrogen afterglow. Whether different modes of excitation do, in fact, produce the same active species is still a matter of some speculation.

POSSIBLE REACTIVE SPECIES IN ACTIVE NITROGEN

As a result of extensive studies on active nitrogen, the reactivity of the glowing gas has been attributed to various species. There is very little doubt that, of the various reactive components that might be present, ground state nitrogen atoms are of primary importance. However, there seems to be conclusive evidence that excited nitrogen molecules may also contribute substantially to the reactivity of the gas.

Wrede (39) demonstrated the presence of nitrogen atoms in active nitrogen by pressure measurements with a diffusion gauge within which atom recombination occurred. The gauge that now bears his name could not distinguish however, between ground state and excited atoms. Positive evidence for the presence of ground state atoms in the afterglow was first obtained from the paramagnetic resonance spectrum of active nitrogen (40). Excited atoms could not be detected by this method if their concentration were less than about 1% of the total atom concentration. The presence of ground state atoms has been confirmed by mass spectrometric studies (41,42) in which the appearance potential of the peak for e/m=14 was found to be about 14.8 eV, very close to the ionization potential of the ground state nitrogen atom (14.545 eV). Again, the method would fail to detect small concentrations of excited atoms.

Tanaka et al (35) were able to estimate, from vacuum ultraviolet absorption data, that ^2P and ^2D excited nitrogen atoms were present in concentrations about 1/500 the concentration of ground state ^4S atoms. Evidence for the presence of excited atoms has also been found by Broida et al (43,44), who observed $^2D \rightarrow ^4S$ emission from solid products condensed at 4.2°K from the nitrogen afterglow. From measurements of the decay of $N(^2P)$, it was found (45) that two-body collisions with N_2 molecules were ineffective in removing energy from ^2P atoms. Instead, three body collisions of the ^2P atom with two N_2 molecules were suggested. However, from the large number of collisions that were calculated, it was inferred that two particles formed a temporary complex prior to the collision with the third.

Milligan et al (46) found evidence for the presence of N_3 in products condensed at 4.2°K from a glow discharge in nitrogen. Although the existence of N_3 was also suggested by Thrush (47), as a product of the flash photolysis of hydrazoic acid, other results from infrared studies of solids condensed from a discharge in N_2, disproved its existence (48). It is likely that if N_3 is present in active nitrogen, its concentration should be negligibly small, since it might be expected to be destroyed rapidly by nitrogen atoms.

Some reactions suggest the possible participation of excited molecules as reactive species in active nitrogen. Willey and Rideal (20) observed a rapid decomposition of NH_3 by active nitrogen and suggested that an excited molecule might be responsible for the reaction. Freeman and Winkler (49) found that active nitrogen formed in a condensed discharge was able to decompose ammonia to an extent only about one-sixth of the total activity of the nitrogen, inferred from its ability to produce HCN from ethylene. They also found that, in the presence of ammonia, active nitrogen was still capable of producing HCN from ethylene and subsequent studies (50) showed that this yield was not reduced relative to that obtained in the absence of NH_3. It was suggested that the species capable of reaction with NH_3 was $N_2(A^3\Sigma_u^+)$ excited to low vibrational levels. Similarly, Kistiakowsky and Volpi (51) found, by mass spectrometry, that no reduction occurred in the concentration of nitrogen atoms when ammonia was added to active nitrogen, although the intensity of its afterglow was thereby reduced. They observed no destruction of NH_3 by active nitrogen formed in a microwave discharge, but small changes in its concentration would be beyond the detection limit of the mass spectrometer.

In their discussion of the possible reactive components in active nitrogen, Evans and Winkler (4) suggested that vibrationally excited ground state N_2 molecules might be the species capable of reaction with ammonia. This was proposed at the time because the life-times of all the known excited molecular states of nitrogen, including the $A^3\Sigma_u^+$ state, had been estimated (52) to be too short to allow their survival in significant concentrations into the reaction zone. It has subsequently been established that the A state has a life-time in the order of tenth of seconds or more, and cannot be ruled out solely on these grounds as a possible reactive species.

The presence of vibrationally excited ground state molecules has been demonstrated directly by their vacuum ultraviolet absorption spectrum (53). A few substances like CO, CO_2, and N_2O, which do not appear to react with nitrogen atoms when added to the Lewis-Rayleigh afterglow, are now believed to deactivate the vibrationally excited species. This effect is usually marked by some quenching of the afterglow at the point of mixing, accompanied by local heating. Kaufman and Kelso (54) observed a strong decrease in the afterglow intensity when N_2O was admitted to active nitrogen from a microwave discharge, but there was a small subsequent increase in the intensity further downstream. The temperature increased at the mixing point, but decreased further downstream. Mass spectrometric analysis of the gas indicated that no N_2O was consumed. The temperature rise was attributed to deactivation of vibrationally excited ground state N_2 molecules by N_2O; the accompanying reduction in the intensity of the afterglow was presumably due to the negative temperature coefficient of the Lewis-Rayleigh afterglow.

When Kaufman and Kelso added nitric oxide to that part of the afterglow which was extinguished by N_2O, and then added N_2O downstream, they found an enhancement in the heat release. They attributed this to the inability of NO to react with the excited molecules and concluded that, in fact, NO produced vibrationally excited nitrogen molecules when it reacted with active nitrogen.

More recent studies (55,56) have indicated that active nitrogen from a microwave discharge can induce emission from N_2O, CO and CO_2, probably as a result of an energy transfer from vibrationally excited molecules. This probably results from a reasonably close resonance match between the fundamental vibrational frequencies of ground state N_2, and those of the receptor gases (55,57). However, the energy associated with vibrationally excited ground state N_2 is quite insufficient to induce reaction with these gases (with the possible exception of N_2O, for which about 1 eV might suffice). On the other hand, vibrationally excited N_2 molecules might well promote reactions that require less than 25 kcal/mole for their initiation, and there is experimental evidence that the dissociation of ozone by active nitrogen is a case in point (58).

Recent spectroscopic observations strongly favour a radiative life-time of the order of 10^{-2} sec, or greater, for the $A^3\Sigma_u^+$ state. The lower limit of 10^{-2} seconds was suggested by Lichten (30), and a value of about 0.07 sec was found by Wright _et al_ (50) and by Dunford (31). Noxon (59) positively identified this species during measurements of the emission of the Vegard-Kaplan bands in the pressure range 20 to 760 torr, and reported a value of about 1 sec for its radiative life-time. This agrees reasonably well with that obtained by Carleton and Oldenberg (60) of 2.0 ± 0.9 sec, and with the more recent value of 0.9 sec reported by Zipf (61). These recent values for the life-time of $N_2(A^3\Sigma_u^+)$ probably favour it over vibrationally excited ground state N_2 molecules, as a possible reactive species in active nitrogen.

In an investigation of the CN radical emission from reactions of active nitrogen with XCN(X=H, Cl, Br, CN), Bayes (62) found that the addition of 2% ammonia quenched the reaction flame completely, while the nitrogen afterglow was only slightly altered. He concluded that ammonia removes the species which initiates the CN emission, and that this species is not involved in the production of the afterglow. After consideration of various possible reactive molecular species in these reactions, Bayes concluded, that $N_2(A^3\Sigma_u^+)$ must be the species that destroys ammonia and produces the CN emission, by the sequence

$$N_2(A^3\Sigma_u^+) + XCN \rightarrow N_2(X^1\Sigma_g^+) + X + CN^*$$
$$CN^* \rightarrow CN + h\nu$$

The participation of electronically excited nitrogen molecules in some reactions of active nitrogen is also indicated by the results obtained with iodine. A blue emission from this system, believed to be due to excited I_2 molecules, was attributed (63) to

$$N + I_2 \rightarrow NI + I$$
$$NI + N \rightarrow N_2(A^3\Sigma_u^+) + I$$
$$N_2(A^3\Sigma_u^+) + I_2 \rightarrow N_2(X^1\Sigma_g^+) + I_2^*$$

The existence of $N_2(A^3\Sigma_u^+)$ molecules in this system was observed by absorption spectroscopy (64), which suggested that this state may have a relatively long radiative life-time.

An efficient energy transfer appears to be associated also with the dissociation of TlI (65). The data indicated a second order reaction, which might occur by,

$$N_2^* + TlI \rightarrow N_2 + Tl^* + I$$

where N_2^* is an excited state with electronic energy up to 9.76 eV.

It is interesting, perhaps, that fluorescent sensitization of Tl was observed in the photo-excitation of Tl in the presence of ammonia (66). The intensity of Tl emission increased with partial pressure of NH_3 and a basic energy exchange from excited ammonia to the Tl atom was assumed.

ESTIMATION OF NITROGEN ATOM CONCENTRATION

A number of methods may be used to estimate the nitrogen atom concentrations. The most commonly used methods have been chemical methods (67,68), mass spectrometry (41), electron spin resonance measurements (69,70), and Wrede gauge measurements (71). Of these, it will suffice here to outline briefly the first three.

The physical methods have certain advantages, such as minimum disturbance of the system, the possibility of measurements *in situ*, and perhaps of measuring the concentrations of several reactive species simultaneously. It has generally been necessary to calibrate such methods against chemical estimations.

Chemical methods have been popular for determining absolute N atom concentrations and were used in the present study. The reaction involved in the estimation must be rapid (to minimize side reactions), it is desirable that it conforms to simple kinetics, with a mechanism that is understood, and it should be readily followed by simple analytical techniques.

Ethylene and nitric oxide are the reactants that have been used most widely for the purpose.

Winkler and his co-workers have studied the reaction of active nitrogen with a variety of hydrocarbons (saturated and unsaturated) and found that, for many reactants, the production of hydrogen cyanide accounted for almost all (>95%) of the nitrogen-containing products of the reaction. The yield of HCN was determined by titration methods. The HCN production, at high hydrocarbon flow rates, was practically constant over a wide range of experimental conditions, and with few exceptions, was independent of the hydrocarbon used. The olefins, particularly ethylene, were found to react rapidly with active nitrogen, and to be convenient for establishing the plateau HCN value for given operating conditions of the active nitrogen system. The plateau HCN value was equated to the nitrogen atom flow rate at the point at which the ethylene was introduced. The reactions were assumed (67) to be,

$$N + C_2H_4 \rightarrow HCN + CH_3\cdot$$

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

When nitric oxide is used to estimate the N atom flow rate, the point of equivalence between the N atom and NO concentrations is determined by visual observation (54). As the flow of NO is increased, the yellow colour of the Lewis-Rayleigh afterglow is at first diminished with gradual development of violet-blue glow (β and γ bands of NO) due to the simultaneous presence of both N and O atoms,

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

$$O + N + M \rightarrow NO^* + M$$

$$NO^* \rightarrow NO + h\nu \quad (\beta, \gamma \text{ bands})$$

On the other hand, when NO is in excess the green "air afterglow" is observed due to the reaction,

$$O + NO \rightarrow NO_2^* \rightarrow NO_2 + h\nu \quad (\text{continuum})$$

The equivalence point, or "endpoint" of the "titration," corresponding to the presence of neither nitrogen atoms nor nitric oxide, is detected by the absence of emission, i.e., a "dark" field of view. The titration is capable of excellent reproducibility when the proper flow lines are employed.

A closely parallel sequence of reactions, with NO_2 as titrant, for the estimation of oxygen atom concentration (72,73) involves the very rapid reaction,

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

accompanied by the green emission of NO_2^* as long as O atoms are in excess; darkness ensues when the NO_2 flow rate is increased to the equivalence point.

These gas phase "titration" methods are independent of the nature of M, the third body, provided it is inert to the reacting species. The intensity of the glow (blue or green) is then directly proportional to the concentrations of the atomic species. The methods have been used a number of times to calibrate physical methods based on, for example, mass spectrometric (74) or ESR (70) estimations.

The two chemical methods, based on plateau HCN yields and on NO titrations, do not give concordant results (67,75). A rather lively controversy therefore developed. The NO titration generally gives a higher value for the N atom concentration than that inferred from the HCN value; the ratio (NO destroyed)/(HCN produced), more simply referred to hereafter as the NO/HCN ratio, may vary from unity to as high as 2.4 as the pressure is increased from 1 to 16 torr. It was suggested (67) that the discrepancy might be due to destruction of NO by both nitrogen atoms and a second species, presumably excited nitrogen molecules, which do not produce HCN from ethylene. Wright *et al* (50) confirmed these results, and found that the ratio NO/HCN was practically independent of nitrogen atom concentration at constant pressure, and that it was also independent of the mode of excitation of molecular nitrogen and of the reaction temperature. Furthermore, the ratio was not affected by the addition upstream of N_2O or CO_2, but depended on the time of decay of active nitrogen. This suggested the reaction of NO with an excited nitrogen molecule that might be formed homogeneously, and perhaps heterogeneously also outside the discharge tube. Since addition of N_2O and CO_2 did not affect the NO/HCN ratio significantly, the energetic species involved in the reaction with NO would have to be electronically excited, rather than vibrationally excited in the ground state, owing to the efficient deactivation of the last by N_2O and CO_2.

From the similarity in the plots of NH_3 (destroyed)/ HCN (produced) and NO (destroyed)/HCN (produced) against HCN yield, Wright <u>et al</u> (50) suggested that both the NH_3 and the NO reactions occur, in part at least, with the same species and this is incapable of forming HCN from ethylene. The species capable of destroying NO was associated with a half-life time of about 8.4×10^{-2} sec, and that responsible for the destruction of ammonia with a half-life of 6.9×10^{-2} sec. These values are similar to the ones reported for the life-time of the $A^3\Sigma_u^+$ state (76,60,77).

However, when chemical estimations of nitrogen atom concentrations are compared with estimations based on physical methods, it appears that the NO titration method gives the more consistent and reliable measure of the N atom concentration. For example, Weyssenhoff and Patapoff (78) found agreement (within ± 10%) between the NO titration values and the N atom concentrations measured by ESR techniques, except at linear velocities several times higher than those commonly used. The nitric oxide titration then gave significantly higher values. This behaviour was attributed to the destruction of NO by a species other than N atoms. Westenberg and de Haas (70) also obtained data with the ESR that supported the validity of the NO titration.

In contradication to these conclusions, Fersht and Back (79) obtained data that supported the limiting yield of HCN from the ethylene reaction as a true measure of the N atom concentration. They added ^{15}NO and ethylene simultaneously to an active nitrogen stream and measured the yields of $^{14}N^{15}N$ and HCN. The nitrogen atom concentration inferred from pure ^{15}NO was about 1.55 times that based on HCN production from ethylene alone. However, in the presence of $^{15}NO/C_2H_4$ mixtures the sum (HCN + $^{14}N^{15}N$) remained almost constant and equalled the value based on HCN from pure ethylene. At relatively higher nitric oxide content, the apparent atom concentration approached the value obtained from pure ^{15}NO. These data were explained in terms of a probable consumption of ^{15}NO by an electronically excited nitrogen molecule incapable of forming HCN from ethylene.

Recently, a mass spectrometric study has been made of the reaction of active nitrogen with ethylene (80). The data suggest that catalytic recombination of nitrogen atoms may be suppressed in the presence of high concentrations of hydrogen atoms, with consequent higher HCN production. When 2% of hydrogen gas was added to the nitrogen stream through a microwave discharge, the yield of HCN from the ethylene reaction increased and little discrepancy remained between the NO and HCN measures of N atom concentration. A reaction mechanism was proposed in which N atoms abstracted H atoms from ethyl radicals, and were thereby consumed without producing HCN. However, there seems no obvious reason why HCN, rather than NH radicals, should not result from the N atom attack on ethyl radicals.* Since the rate constant for the ethylene reaction is about three orders of magnitude smaller than that for the NO reaction, the ethylene reaction might not compete with NO in a simple way in the experiments in which ($^{15}NO + C_2H_4$) mixtures were used (79).

A seemingly convincing physical method for measuring the absolute N atom concentration (82) is based on measurement of the pressure decrease that result when the atoms recombine

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* The reaction of N atoms with ethyl radicals is probably very fast, as it is with methyl radicals (81), since there is, in general, no evidence for the survival of appreciable concentrations of alkyl radicals in the reactions of active nitrogen with hydrocarbons.

in an isolated portion of the dissociated gas stream. Data obtained with this method were in excellent agreement with values obtained by the NO titration.

A recent study (83) with N atoms has suggested that the ground state N atoms are incapable of reacting efficiently with C_2H_4, but may react readily with NO. It was tentatively concluded that the primary reaction of C_2H_4 with active nitrogen might be with either an excited nitrogen atom, or with an excited nitrogen molecule.

In summary, there is little doubt that the nitric oxide titration gives a true estimate of the N atom concentration, in an active nitrogen stream, but it seems likely that the atom concentration might not represent the total chemical activity of active nitrogen formed under all conditions. Part of the activity might reside in electronically and vibrationally excited molecules, in ions, and perhaps to some slight extent in excited atoms.

REACTIONS OF ACTIVE NITROGEN

Although the early studies on the reactions of active nitrogen were mainly qualitative, they delineated a wide field for interesting further investigations. Strutt in his early studies showed that active nitrogen reacts with metals to form nitrides, with nitric oxide to form some dioxide, with white phosphorus to form red phosphorus, with carbon disulfide to form polymers, with hydrocarbons to form cyanogen and hydrogen cyanide, and with many other compounds (2). Most of these reactions were accompanied by a characteristic luminosity, the spectrum of which was different in structure from that of the afterglow (e.g., hydrocarbon reactions were accompanied by the CN radical emission).

Lewis (1) observed the excitation of metallic lines of mercury and of aluminum (from the electrodes) in the spectrum of the afterglow. Strutt and Fowler (84) found that active nitrogen could excite the spectra of sodium and mercury iodide, and that it emitted its energy more quickly at lower temperatures.

Willey and Rideal (20) observed that ammonia was rapidly decomposed by active nitrogen. Dixon and Steiner (85) noted later that the reactivity was low, in spite of a marked weakening of the afterglow, and they were not able to detect the NH radical spectroscopically. They also found that active nitrogen reacts with atomic hydrogen to produce negligibly small quantities of ammonia (85,86), and with molecular hydrogen to produce hydrazine (85,86) in small amounts. The need for a third body in these reactions was confirmed, when the yield of ammonia increased fourfold in the presence of a metal surface (85) that stabilized the reaction products.

Spealman and Rodebush (72) studied the reaction of NO and NO_2 with both active nitrogen and atomic oxygen. They observed that the yellow nitrogen afterglow gave way to a blue glow at low flow rates of NO and NO_2, and that a greenish-yellow glow due to excited NO_2 was produced at higher flow rates. The green glow disappeared when a large excess of NO_2 was used, but did not disappear at any flow rate of NO. The disappearance of the yellow nitrogen afterglow was attributed to

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

The appearance of the greenish-yellow glow was associated with the reaction

$$O + NO \rightarrow NO_2$$

In excess NO_2, the glow was quenched and they postulated the reaction

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

A systematic study of the reactions of active nitrogen was started in 1949 by Winkler and his associates. Both organic and inorganic reactants have been examined kinetically, not only to evaluate the kinetic parameters, but to obtain information, if possible, on the nature of active nitrogen itself, in particular the nature of the chemically active species present in the glowing gas. A large number of reactions have now been studied, and the literature on the chemistry of active nitrogen has grown apace. Many of these reactions involve organic molecules, and have rather peripheral significance in relation to the present investigation. Consequently, the review that follows will be concerned mainly with reactions of active nitrogen with inorganic reactants, and indeed, with only some of these. However, it will be useful for further reference to summarize the main features of the reactions between active nitrogen and organic reactants. Fortunately, this can be done without recourse to a great deal of detail about the individual reactions. With inorganic reactants, the thread of common behaviour is much less pronounced.

Reactions of active nitrogen with organic substances

In spite of the many studies that have been made, present understanding of these reactions is limited. In general, HCN is the main nitrogen-containing reaction product. In some reactions it may constitute practically all of the condensable products. Frequently, only traces of nitrogen-hydrogen products are detected, which suggests that the main reaction involves direct attack upon the carbon atom, rather than hydrogen abstraction. The reactions are accompanied by emission in the reaction zone, which indicates the presence of electronically excited species such as CN·, CH·, and NH· radicals.

The saturated hydrocarbons that have been investigated include methane, ethane (87,88,89,81), propane (87,81,90), the butanes (91), and neopentane (92,81). The major, and sometimes the only nitrogeneous product of these reactions was hydrogen cyanide. Smaller yields of hydrogen and unsaturated hydrocarbons relative to hydrogen cyanide were also found. With methane and ethane as reactants at elevated temperatures, the HCN yield increased rapidly with hydrocarbon flow rate, practically eliminating the "induction" effects noted at room temperature. Gartaganis and Winkler (88) suggested that the effect appeared to be due to attack of CH_4 and C_2H_6 by H atoms, since the initial low HCN yield could be markedly increased by the addition of appropriate amounts of atomic hydrogen to the system. This effect was later noticed also by Herron (80).

The reactions of active nitrogen with unsaturated hydrocarbons (87,93,94) were found in general, to be faster than those with the corresponding saturated compounds. The reactant (hydrocarbon or active nitrogen) present in lesser amount was completely consumed. Hydrogen cyanide was the main reaction product, accompanied by small amounts of cyanogen and saturated hydrocarbons. The yield of HCN was found to increase with hydrocarbon flow rate to the attainment of a limiting ("plateau") value. With ethylene as reactant, it was confirmed that the reaction proceeded with complete consumption of nitrogen atoms in the presence of relatively small excess of ethylene. The hydrogen cyanide yield from this reaction was taken as a measure of the prevailing N atom concentration in the reaction system.

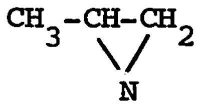
The reactivities of cycloparaffins are quite low at room temperature (about 10^{-16} cc/molec-sec), and it increases in the order cyclopropane<cyclobutane<cyclopentane (95). The main products were HCN and C_2H_4, and the relative proportions of C_2H_4 to HCN increased with the number of carbon atoms in the ring and with temperature. No limiting yields of HCN were obtained at room temperature, and were obtained at 350°C only with cyclobutane and cyclopentane.

The reactions of active nitrogen with a number of hydrocarbon derivatives have also been studied. These include methylamine (96), ethylamine (97), methyl cyanide (98), mercury diethyl (99) and alkyl halides (100). Studies have also been made with compounds such as cyanogen (101), silane and methyl silanes (102), azomethane (103), and CS_2 (104). Kinetic data have been obtained with only a few of these, and they need not be considered further.

Violet emission of the CN radical is quite intense in the presence of olefins and alkyl halides. Spectral investigations have revealed that fairly high electronic excitation may be involved in some of the reactions, and Sester and Thrush (105) have suggested that the excitation may be due to $N_2(A^3\Sigma_u^+)$ molecules, or due to a precursor having a CN bond.

The participation of $N_2(A^3\Sigma_u^+)$ molecules, rather than N atoms, in the primary steps of the reaction of methane, ethane and cyclopropane has been suggested (87,106). The addition of ammonia to the active nitrogen above the hydrocarbon inlet resulted in a decrease in HCN production with a simultaneous reduction of the CN emission. An increase of hydrocarbon flow rate resulted in an increased rate of HCN formation, with a concomitant decrease in the NH_3 consumption. This suggested that a species other than N atoms might initiate these reactions. Since ammonia is considered to react with excited nitrogen molecules only (49,50), the inhibiting effect of ammonia indicates that these reactions probably involve initiation by electronically excited nitrogen molecules. Furthermore, the HCN production from methane and ethane, at 400°C, showed an "induction" effect at relatively short reaction times, but attained a value that was equal to that from the ethylene reaction when the hydrocarbon flow rate and reaction time were sufficiently increased. This suggested a direct attack of N atoms on alkyl radicals formed in a rapid reaction of the hydrocarbon with H atoms produced by the initiating step. The complexity of the reaction path was reflected in a rapid change in slope of the Arrhenius plots corresponding to different controlling steps in different ranges of temperature (81).

Evans et al (107) reviewed the reactions of active nitrogen with various organic compounds and proposed a "unified" mechanism. Using as an example the reactions of propane, propylene and propyl chloride, they suggested that a similar collision complex might be formed in these reactions, of the type



$$\underset{N}{CH_3\text{-}CH\text{-}CH_2}$$

or

$$\underset{N}{CH_3\text{-}CH\text{-}CH\text{-}Cl}$$

The authors further suggested that the interaction of the p-electrons of the carbon atom and the nitrogen atom allow the close approach of the latter without surmounting a large potential barrier. The complex so formed may then decompose with the formation of HCN and a radical (plus HCl with propyl chloride)

$$(N\cdot C_3H_6) \longrightarrow HCN + C_2H_5\cdot$$

This radical may then lose a hydrogen atom or react further with active nitrogen. Both of these reactions are expected to be very fast. Since the life-time of the complex has to be sufficient to allow the hydrogen migration, its stability will evidently influence the reaction rate.

Herron (108) postulated a generalized mechanism for the reactions of nitrogen atoms with several olefins. He emphasized the importance of hydrogen atom reactions in suppressing the catalytic recombination of nitrogen atoms, thereby leading to an increase in the HCN production. The reaction scheme was

$$\text{Active nitrogen} + \text{Olefin} \rightarrow \text{Products} + \text{H} \quad .....(1)$$

$$\text{H} + \text{Olefin} \rightarrow \text{R}\cdot, \ (\text{R}\cdot\text{=Radical}) \quad .....(2)$$

$$\text{H} + \text{R}\cdot \rightarrow \text{RH} \quad .....(3)$$

$$\text{N} + \text{R}\cdot \rightarrow \text{Olefin} + \text{NH}\cdot \quad .....(4)$$

$$\text{N} + \text{NH}\cdot \rightarrow \text{N}_2 + \text{H} \quad .....(5)$$

For short reaction times, reaction (4) predominates over (3) and any olefin lost in reaction (2) is regenerated in reaction (4), which is simultaneously accompanied by N atom recombination, reaction (5). However, at longer reaction times, reaction (3) may become significant, and lead to a net loss of olefin other than by reaction (1), thus increasing the apparent rate constant. It was suggested that true rate constants may be obtained by plotting the apparent rate constant against the ratio of [olefin] / [N] and extrapolating to zero olefin concentration, thus suppressing subsequent hydrogen atom side-reactions. The apparent rate constant, which increased with H atom addition for a given [olefin] / [N] ratio, yielded an unaltered value for the extrapolated rate constant. From the similarity between the rate constants for the nitrogen atom and hydrogen atom reactions with olefins, Herron concluded that the primary step in these reactions might be identical, perhaps the addition to the least substituted carbon atom of the double bond to form an excited radical from which, after subsequent reactions, stable products may emerge.

It is interesting, perhaps, that Armstrong and Winkler (12), in an earlier study, found that the yield of HCN production from ethylene was greater when active nitrogen was produced by a discharge through ammonia than through molecular nitrogen. It is likely that the hydrogen atoms present in the effluent from the discharge promoted HCN production in a manner similar to that suggested by Herron.

It is evident from the foregoing summary of some of the main characteristics of active nitrogen reactions with organic molecules, that the mechanisms of such reactions are not yet well understood. The saturated hydrocarbons seemingly require that the reaction be initiated by an excited nitrogen molecule, followed, perhaps, by fast N atom attack on free radicals. The reaction of nitrogen atoms with methyl or ethyl radicals is undoubtedly fast, and provides an important source of HCN. This might explain, in part at least, the nearly constant limiting yield of HCN from a variety of organic substances.

Such radicals will be abundant in systems where fragmentation of the parent hydrocarbon occurs, and determination of rate constants or individual processes will be difficult simply because one substance may participate in more than one elementary reaction.

Reactions of active nitrogen with inorganic substances

The many studies of these reactions have encompassed as reactants a number of elements (e.g., Hg, Al), atoms (e.g., N, H, O) and molecules (e.g., H_2, O_2, HBr, H_2S, CS_2, NO, NO_2, NH_3, PH_3, etc.). In general, they do not exhibit common characteristic features. For the purpose of the present discussion, only a rather limited number of these reactions need be considered.

(i) The recombination of nitrogen atoms

Probably the most extensively investigated of the reactions of nitrogen atoms is their homogeneous recombination,

$$N + N + M \rightarrow N_2 + M$$

The rate constants have been determined by a variety of methods, but generally in flow systems, and frequently by monitoring the change in N atom flow rate by the NO titration. It is generally agreed that this process is second order in respect of nitrogen atoms. The agreement between the various data is generally good (68,109,110), while discrepancies that exist might be explained by the probable contamination of the nitrogen gas, particularly with water vapour. Kretschmer and Petersen (71) added water to the nitrogen before it entered the discharge tube, followed by oxygen downstream, and found an enhanced rate of recombination. They ascribed the increased rate to a chain mechanism

$$H + O_2 + M \longrightarrow HO_2 + M$$

$$N + HO_2 \longrightarrow NH + O_2$$

$$N + NH \longrightarrow N_2 + H$$

Rate constants for the homogeneous recombination of N atoms vary from $1.2x10^{-32}$ to $10^{-31}cc^2/molec^2$-sec with nitrogen as third body. Herron <u>et</u> <u>al</u> (111) used helium as a third body, and reported a rate constant about 8 times smaller than the one he obtained in the presence of N_2. On the other hand, Campbell and Thrush (112) found that helium was more efficient than either argon or nitrogen. There remains some disagreement also about the variation of the rate with temperature. Herron <u>et</u> <u>al</u> (111) did not observe any temperature dependence in the range 195-300°K, while Campbell and Thrush (113), and Clyne and Stedman (114) reported a small negative activation energy (-975 ± 140) and (-1000 ± 300)cal/mole, respectively.

The homogeneous recombination is almost always accompanied by a heterogeneous recombination, believed to be first order in nitrogen atoms. It is rather difficult to assess the order and importance of the wall effects, since it is difficult to reproduce surface conditions. Evenson and Burch (115) found that the recombination coefficient on quartz ranged from $7x10^{-6}$ to $5x10^{-4}$. It decreased with increase in O_2 content in the discharged nitrogen, and the rate seemed to be even slower than that corresponding to a third order mechanism. On the other hand, Clyne and Stedman (114) observed a second order ($N + N \longrightarrow N_2$) heterogeneous recombination of N atoms to be involved on a "clean" glass surface, but this seemed to disappear when the reaction tube was "poisoned" with phosphoric acid. It is generally accepted that the heterogeneous reactions are almost completely suppressed above about 2 torr, especially when the wall of the reaction vessel has been "poisoned" with, for example, H_2O, metaphosphoric acid, concentrated sulphuric acid, etc.

The study of afterglow kinetics has included an evaluation of the homogeneous recombination rate constant. This was based on estimates of N atom concentrations and afterglow intensity. The intensity of the Lewis-Rayleigh afterglow, according to the recombination kinetics now accepted, is proportional to the total concentration of the carrier gas and to the square of the concentration of the ground state nitrogen atoms. Lord Rayleigh (116) who first proposed this relation, suggested a somewhat smaller dependence on total pressure above 0.1 torr. Berkowitz, Chupka and Kistiakowsky (41) determined the N atom concentration mass spectrometrically, and found that the intensity of the afterglow was approximately proportional to $[N]^2 [M]$ over the range 0.25 to 1 torr. On the other hand, Young and Sharpless (117) found the intensity of the afterglow in pure nitrogen to be proportional to $[N]^2$, and independent of total pressure in the range 1 to 10 torr. It would appear, however, that a decrease in the pressure of the molecular nitrogen, at constant N atom concentration, does correspond to a reduction in the intensity of the afterglow. Decreasing the concentration of the nitrogen atoms at constant concentration of the molecular nitrogen results in a decrease in afterglow intensity, which is proportional to the square of the decrease in partial pressure of the active species. It appears likely that more work at lower pressures (below 1 torr) is needed, since at higher pressures the efficient electronic quenching by N_2 will be the predominant process (118).

(ii) Reaction with atomic and molecular hydrogen

Lewis (119) found that active nitrogen reacted with atomic hydrogen to yield ammonia. A later study by Steiner (86) confirmed the formation of NH_3 as well as a small production of hydrazine. He postulated the mechanism

$$N + H + M \longrightarrow NH + M \qquad .... (1)$$

$$H + H + M \longrightarrow H_2 + M \qquad .... (2)$$

$$NH + H_2 + M \longrightarrow NH_3 + M \qquad .... (3)$$

It was previously mentioned that the necessity for a third body in this reaction (as well as in the reaction with molecular hydrogen) was realized by Dixon and Steiner (85), who obtained an increase in the ammonia production when the reaction occurred in the presence of a metal surface. They also suggested that hydrazine was formed by reaction (1), followed by

$$NH + H + M \longrightarrow NH_2 + M$$

and

$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M$$

Dixon and Steiner found that the ammonia production was first order in respect of the hydrogen atom concentration, and that the steady state concentration of NH radicals was very low. Rice and Freamo (120) in a later study, also failed to detect the NH radical in a similar system.

A more recent spectroscopic investigation of the N-H system (121) revealed that in addition to the N_2 First Positive emission ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$), the Second Positive System ($C^3\Pi_u \rightarrow B^3\Pi_g$) and the NH($A^3\Pi \rightarrow X^3\Sigma^-$) bands were observed in emission. The observed bands of this molecule corresponded to an excitation level for the NH($A^3\Pi$) state of 3.5 eV. The suggested mechanism involved the reaction

$$N(^4S) + H(^2S) \longrightarrow NH(^5\Sigma^-)$$

where $^5\Sigma^-$ is an unstable state that crosses over into the $A^3\Pi$ configuration. The formation of $N_2(C^3\Pi_u)$, and also $NH(A^3\Pi)$, in vibrational levels from which transitions were observed, was explained by

$$NH(A^3\Pi)_{v=high} + N_2(B^3\Pi_g)_{v=12} \longrightarrow (N_3H \text{ unstable})$$
$$(N_3H) \longrightarrow NH(A^3\Pi)_{v=0,1} + N_2(C^3\Pi_u).$$

This mechanism was criticized by Mannella (122) owing to the uncertainty involved in the cross-over from the $^5\Sigma^-$ state to the vibrational levels of the $NH(A^3\Pi)$ state. The former state is basically a repulsive one and there is no indication that the potential energy curve of the $A^3\Pi$state crosses that of the $^5\Sigma^-$ at its minimum. (This is unlike the $^5\Sigma_g^+$ and $B^3\Pi_g$ states of nitrogen that are involved in the production of the afterglow, and that cross slightly below $D(N_2)$ at a point where the $^5\Sigma_g^+$ can have a minimum). Mannella suggests that ground state atoms of nitrogen and hydrogen react to form ground state $NH(X^3\Sigma^-)$ molecules, while $NH(A^3\Pi)_{v=0,1}$, from which emission was observed, might be formed by

$$N_2(B^3\Pi_g)_{v=12} + NH(X^3\Sigma^-) \longrightarrow NH(A^3\Pi)_{v=0,1} + N_2(A^3\Sigma_u^+)_{v=0}$$

This is plausible since the $(B^3\Pi_g)_{v=12}$ transition to the A state is associated with about 3.6 eV, compared with 3.5 eV required to form $NH(A^3\Pi)$. On the other hand, the formation of the $C^3\Pi_u$ state, which is the upper state of the Second Positive System of N_2, requires 11.2 eV for its excitation. It was suggested that vibrationally excited $A^3\Sigma_u^+$ molecules might interact with $NH(A^3\Pi)$ radicals, in accordance with

$$N_2(A^3\Sigma_u^+)_{v=6-9} + NH(A^3\Pi)_{v=0,1} \longrightarrow NH(X^3\Sigma^-) + N_2(C^3\Pi_u)_{v=0,1}$$

This would be energetically neutral, with the excitation energy associated with the $N_2(A^3\Sigma_u^+)_{v=6-9}$ state (7.4 - 7.8 eV·). This mechanism is compatible with the experimental observations; it does not involve assumptions about the potential energy curve of NH that might be required, and it does not involve unstable intermediates.

The related reaction of molecular hydrogen with active nitrogen did not seem to occur in the system investigated by Lewis (119). However, a more thorough investigation by Steiner (86) showed that traces of hydrazine were formed. He postulated the mechanism

$$N + H_2 + M \longrightarrow NH_2 + M$$

$$NH_2 + NH_2 + M \longrightarrow N_2H_4 + M$$

Varney (123) investigated this system, using active nitrogen produced in a glow discharge, in an effort to determine the influence of possible ions in active nitrogen on the chemical activity of the gas. In contrast to Steiner, tests for hydrazine were negative. Instead, a dark brown crystalline material was condensed, which appeared to be unstable at room temperature. Mass spectrometric analysis showed no product other than NH_3. Since changes in the electrical parameters of the discharge left the yield of NH_3 unaltered, Varney concluded that no ionic species was involved in the reaction. However, it was not established whether the species responsible for the reaction was atomic nitrogen or a metastable molecular state.

Kistiakowsky and Volpi (51) also investigated the H_2 active nitrogen system with a mass spectrometer and found no significant reaction either at room temperature or at about 250°C. They estimated an upper limit of 10^{-16}cc/molec-sec for the rate constant. The presence of H_2 did not cause any visible change in the afterglow, neither was the ratio of the ion currents, M14/M28, appreciably affected. Ion currents corresponding to mass 15 or 16 were detected when as much as 10% of H_2 was present in the active nitrogen stream. However, the authors doubt that the appearance of the ions of a product in a mass spectrometer is a sensitive criterion for its presence, especially with H_2, because of the background ions (M16,17). Varney's observations were attributed to diffusion of hydrogen into the discharge region, which could result in a reaction between atomic nitrogen and atomic hydrogen. Kistiakowsky and Volpi concluded that the reaction with H_2,

$$N + H_2 \longrightarrow NH + H$$

must be associated with an activation energy in excess of 15kcal/mole. This is perhaps not surprising, in the view of its apparent endothermicity of about 16kcal/mole. On the other hand, the reaction

$$N + H_2 + M \longrightarrow NH_2 + M$$

requires an appreciable activation energy, although it is exothermic, since its rate constant is at least an order of magnitude lower (10^{-33} cc^2/molec^2-sec) than the triple collision frequency.

(iii) Reaction with atomic and molecular oxygen

The reaction of active nitrogen with oxygen atoms may occur when oxygen, even in traces, is present as an impurity in molecular nitrogen subjected to a discharge, or when oxygen-containing compounds are introduced into an active nitrogen stream. The reaction may also be studied by mixing streams of atomic oxygen and active nitrogen, formed in separate discharges. The reaction is presumably a termolecular process

$$N + O + M \longrightarrow NO + M \qquad .... \ (1)$$

A rate constant of the order of $\sim 3\times10^{-32}$ cc^2/molec^2-sec has been obtained for the reaction (54). This value lies between the one found for the recombination of oxygen atoms and that for the recombination of nitrogen atoms. Reaction (1) is responsible for the blue afterglow, i.e., the emission of the β, γ and δ band system of NO, downstream from discharges of N_2 in the presence of a trace of oxygen. This has been convincingly demonstrated by Kaufman and Kelso (54) who studied the emission spectrum of a discharge through ^{14}NO and ^{15}NO, and measured the isotope shifts of the bands. When ^{15}NO was introduced into active nitrogen, only the bands of ^{14}NO were observed. They concluded that the emission must be due to reaction (1) to produce excited NO, which subsequently radiates back to the ground state. To what extent the recombination produces excited states of NO (e.g., $B^2\Pi$, $A^2\Sigma$, $C^2\Sigma$) which either radiate or are deactivated by collisions is still unknown.

The corresponding reaction with molecular oxygen is a second order reaction and does not proceed to an appreciable extent at room temperature. Clyne and Thrush (124) suggested that the mechanism was

$$N + O_2 \rightarrow NO + O \qquad \ldots. \ (1)$$

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

They measured the intensity of the "air afterglow" (due to NO_2^*) to elucidate its kinetics. Since not all the NO formed in reaction (1) was consumed by reaction (2), both NO and oxygen atoms were present, thereby enabling the estimation of NO by measuring the intensity of the "air afterglow" with a photomultiplier cell which was previously calibrated with known amounts of NO added to an active nitrogen stream. They reported a rate constant of the order 8.3x10^{12} exp (-7100/RT) cc/mole-sec in the temperature range 412 to 755^{o}K.

Mavroyannis and Winkler (125) followed the maximum oxygen atom production during the reaction by measuring the amount of N_2O_3 produced when the reaction was stopped with an excess of NO_2. They found close correspondence between the oxygen atom production and the maximum amount of HCN produced from an ethylene-active nitrogen system under the same experimental conditions. On the other hand, Clyne and Thrush (124) observed that the maximum production of oxygen atoms corresponded to the NO titration value for active nitrogen. Since the NO/HCN ratio estimated by Mavroyannis and Winkler was greater than unity, there was obviously a discrepancy between the two studies.

In a recent study, Vlastaras and Winkler (126) resolved the disagreement when they followed the maximum O atom production by both the N_2O_3 method and the NO titration. Their experiments showed that the analytical method based on measuring the N_2O_3 yield in the presence of excess NO_2 was valid only when adequate reaction time was permitted for the NO + NO_2 reaction to go to completion. When this was taken into account the N_2O_3 method yielded a rate constant of 3.8x10^{12} exp(-7000/RT) cc/mole-sec, in good agreement with the value reported by Clyne and Thrush.

A recent study of the reaction in which ESR was used to estimate the oxygen atom production in the temperature range between 300-910°K, gave a rate constant of 1.41×10^{13} $\exp(-7900\pm200/RT)$ cc/mole-sec (127). This is in excellent agreement with the value previously reported by Kaufman and Decker (128), ($1.7\times10^{13}\exp(-7500/RT)$ cc/mole-sec), and considerably different from the results recorded above. The reasons for the differences observed have yet to be resolved.

(iv) Reaction with ammonia

This reaction was qualitatively investigated by Willey and Rideal (20), who observed that ammonia was rapidly decomposed by active nitrogen to form hydrogen and nitrogen as the reaction products. Dixon and Steiner (85), in a fruitless attempt to detect the NH radical spectroscopically, concluded that the reaction does not proceed to an appreciable extent, in spite of the marked weakening of the yellow afterglow that occurred in the presence of ammonia. Ammonia was decomposed in their system to an extent of about 0.04×10^{-6} to 1.55×10^{-6} mole/sec as the flow rate of ammonia was increased from 6×10^{-6} to 41×10^{-6} mole/sec.

It was recognized by Willey and Rideal that the ammonia reaction was not readily explained as a nitrogen atom reaction and they suggested that it might involve excited nitrogen molecules. This was supported in a more recent study by Freeman and Winkler (49), in which it was found that, although NH_3 diminished the intensity of the nitrogen afterglow produced by a condensed discharge, it did not extinguish it. No hydrazine was detected in the reaction products over the temperature range -5 to 440°C and hydrogen and nitrogen were assumed to be the only products. At about 70°C, the amount of NH_3 decomposed increased with ammonia input to a limiting value, which was only 1/6 of the N atom content of the active nitrogen, inferred from the maximum HCN yield in the C_2H_4 reaction. At temperatures above about 200°C, the extent of NH_3 decomposition was more extensive as the NH_3 flow was increased. This was shown to be due, in all probability, to H atom reaction at the higher temperatures. Freeman and Winkler concluded from their observations that the NH_3 reaction involved some species in active nitrogen other than N atoms. They suggested, therefore, that active nitrogen contained at least two reactive species, one of which was capable of reacting with ammonia, while the other, or both, might react with ethylene.

Kistiakowsky and Volpi (51) investigated the NH_3 reaction with a mass spectrometer and found it to be relatively slow in the temperature range 300 to 600°K. They estimated an upper limit for its rate constant to be of the order of 10^{-16}

cc/molec-sec. The ratio of the ion currents M14/M28 was unaffected in the presence of NH_3, and the effluent concentration of NH_3 was practically the same with and without active nitrogen from a microwave discharge. They suggested that the apparent slowness of the reaction might be due to the endothermic (about 20kcal/mole) reaction,

$$NH_3 + N \rightarrow NH + NH_2$$

while the process

$$NH_3 + N \rightarrow N_2 + H_2 + H$$

does not conserve spin. From the change in the intensity of the afterglow in the presence of NH_3, Kistiakowsky and Volpi concluded that the reaction involved excited nitrogen molecules, the emitters of the afterglow. Such a reaction could well be an inelastic collision during which the nitrogen molecule might undergo a triplet→singlet transition (e.g., $B^3\Pi_g \rightarrow X^1\Sigma_g^+$) and the ammonia a corresponding singlet → triplet transition.*

Further evidence that the destruction of NH_3 is not initiated by N atoms was provided by Herron <u>et al</u> (111), who observed that addition of excess NH_3 to active nitrogen of microwave origin does not affect the ability of the latter to destroy nitric oxide. It has also been established by Wright and Winkler (87) that the addition of NH_3 to an active nitrogen stream from a condensed discharge, wherein appreciable decomposition of NH_3 was observed, did not decrease its capacity to destroy NO, nor its ability to produce HCN from ethylene.

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* Duncan (129) has shown that the U.V. absorption of NH_3 is due to several electronically excited states, some of which may be triplet.

Results obtained by Kelly and Winkler (130) indicated that the excited nitrogen molecules responsible for the destruction of ammonia were probably formed during homogeneous decay of nitrogen atoms, mainly between flashes in the discharge tube of a condensed discharge through nitrogen. However, appreciable destruction of NH_3 was observed only in active nitrogen produced by a condensed, rather than a microwave discharge. This suggests that the production of excited molecules might also depend on the mode of excitation of the nitrogen. On the other hand, if the excited molecules are formed during homogeneous decay of ground state nitrogen atoms, their concentration should be proportional to the square of the N atom concentration, and should be much lower with a microwave discharge which generally yields quite low flow rates of active nitrogen.

Wright and Winkler (131) studied the reaction in a "poisoned" condensed discharge system that produced relatively high concentration of N atoms, and with which ammonia was decomposed to an easily measurable extent. In an effort to calculate a rate constant for the reaction, they terminated the reaction in the gas phase, after different reaction times, by admitting an excess of C_2H_4 to the reaction mixture. The rate constants that were calculated were assumed to correspond to overall reaction,

$$N_2^* + NH_3 \longrightarrow NH_3^* + N_2 \longrightarrow \text{products} + N_2$$

where both N_2^* and NH_3^* represent excited molecules. The average rate constant for short reaction times and low initial flow rates of NH_3 was $3.7\text{x}10^{-14}$cc/molec-sec. However, consistently lower rate constants were obtained for higher flow rates of NH_3 at longer reaction times. It was suggested that this decrease might indicate, some formation of N_2^*, responsible for the decomposition of NH_3, by homogeneous recombination along the reaction tube.

Dunford (31) has suggested that ammonia is destroyed almost entirely by $N_2(A^3\Sigma_u^+)$ formed in the condensed discharge. His study indicated a rapid decomposition, the extent of which became practically independent of NH_3 flow rates above $2\text{x}10^{-6}$ mole/sec. A perceptible increase in decomposition of ammonia occurred when it was added to a point close to the discharge and no plateau of destruction was observed even with NH_3 flow rates above $10\text{x}10^{-6}$ mole/sec. Values for the decomposition of NH_3 ranged from 0.1 to about $1.1\text{x}10^{-6}$ mole/sec corresponding to the longest and shortest distance from the discharge, respectively. The nitrogen atom concentrations quoted by Dunford show that the total number of nitrogen molecules (ground state and excited) formed by atom recombination between the inlet jet of NH_3 and the trap, was much larger than the number of NH_3 molecules decomposed over the same decay distance. Since NH_3

destruction was attributed to $N_2(A^3\Sigma_u^+)$ molecules, it was inferred that only a small concentration of these molecules was formed by the homogeneous recombination of the nitrogen atoms, in the reaction tube and furthermore, that they survive in appreciable concentrations, for considerable distances downstream.

The initial attack by active nitrogen on ammonia is apparently controlled by the production of excited molecules. This is generally true of substances that react with active nitrogen and for which direct reaction with N atoms is endothermic. For example, the reaction of active nitrogen with various paraffins is probably initiated by N_2* molecules; the fragments so produced then may react rapidly with nitrogen atoms. If ammonia is added to such a system, it quenches N_2* molecules and so inhibits the reaction. This is consistent with the effects of NH_3 on the methane and ethane reactions (87), mentioned previously, in which HCN production and the CN emission were both drastically suppressed. An important aspect of this mechanism, on which information is yet lacking, is the efficiency of the observed transfer of energy to the NH_3 molecules.

(v) Reaction with sulphur, carbonyl sulphide, and sulphur dioxid

The pioneering work of Strutt (2) indicated that two products, one yellow, one blue, are obtained when sulphur is sublimed into a stream of active nitrogen. He suggested that these were S_4N_4 and $(SN)_x$, respectively. These products, together with a red compound, S_5N_2, were also obtained when sulphur vapour was introduced into the discharge tube (132).

In a recent study by Bett and Winkler (133) the system seemed to be best described in terms of three zones of stoichiometry as the reaction progressed. In region I when the concentration of S atoms was lower than that of N atoms, there was deposited a golden-yellow transparent product of relatively low N content. In zone II, when the N atom concentration was approximately equal to that of the S atoms, a transparent blue reaction product was obtained, in which the N:S ratio was considerably higher. Zone III, when S atoms were in excess of N atoms, yielded a product of almost constant N content, which was lower than the prevailing nitrogen atom concentration in the system. As the flow rate of S atoms was increased, the reaction product in this zone changed from blue to brown. By exposing the products from the different zones to the active nitrogen stream, it was found that they were all practically inert to it. Infrared absorption analysis confirmed the presence in the products of plastic sulphur, S_4N_4 and possibly S_5N_2.

The reaction was accompanied by a blue reaction flame that became more pronounced with increasing sulphur atom flow rate. The yellow nitrogen afterglow, which was still apparent in zone I, gave way to the blue emission in zones II and III. A subsequent spectrographic study confirmed the presence of NS bands. Since, under certain conditions, the flame did not reach the wall of the reaction vessel, Bett and Winkler concluded that there must be a region between the flame and the wall within which both S and N atoms exist without yielding the blue emission. This suggested that homogeneous reaction of N with S atoms was not the source of excitation of this emission. Pannetier _et al_ (134) suggested the participation of $N_2(C^3\Pi_u)$ in the excitation process. However, since this species is of negligible concentration in the Lewis-Rayleigh afterglow, it would seem that one of the lower excited states of the N_2 molecule must be responsible for such an energy exchange, if it does occur.

The following mechanism was proposed by Bett and Winkler, on the assumption that the N atom concentration was given by NO titration values:

$$N + S_2 + M \longrightarrow NS_2 + M \quad .... \ (1)$$

$$N + NS_2 \longrightarrow 2NS \quad .... \ (2)$$

$$N + NS \longrightarrow N_2 + S \quad .... \ (3)$$

$$NS + NS \longrightarrow N_2 + S_2 \quad .... \ (4)$$

$$SN + wall \longrightarrow stable\ products \quad .... \quad (5)$$

$$NS + NS + M \longrightarrow stable\ products \quad .... \quad (6)$$

If atom reactions such as N + S + M are assumed to be relatively unimportant, the data correspond to reaction of four N atoms per S_2 molecule to form a stable product. Under the conditions of excess nitrogen atoms, reaction (1) consumes all the S_2 molecules, while the residual N atoms immediately form NS by reaction (2), to be lost subsequently by reaction (3). No stable product (other than S) was observed, under these conditions, and Bett and Winkler concluded that reaction (3) must be much faster than reactions (5) and (6). On the other hand, when the N atom concentration is no longer greater than four times that of the S_2 molecules (zone II), reaction (3) is presumably not completed and residual NS radicals may then undergo reactions (4), (5) and (6) to form stable products. Further increase in the S_2 flow rate is accompanied by a concomitant increase in the stable reaction products, with the attainment of a plateau when the maximum conversion of N to NS by reactions (1) and (2) has been reached. The fraction of NS radicals which appears as S-N stable compounds will then be determined by the relative rates of reactions(4), (5) and (6). From a plot of the nitrogen reacted against S atom flow rate, it appeared that the maximum production of NS (i.e., zone III) was obtained when the N atom concentration was about twice that of S_2. However, this would require that reaction (1), which presumably requires a third body, should be faster than reaction (3). This is unlikely at a pressure of 3 torr.

It is perhaps interesting that if the maximum HCN production from ethylene is assumed to be a measure of the N atom concentration, two N atoms are lost for each S_2 molecule before stable products are formed. It was suggested that the reaction,

$$N + S_2 \longrightarrow NS + S \qquad .... (7)$$

instead of reactions (1) and (2), may then account for the results. However, for the maximum yield of stable products (zone III) to be obtained when the flow rate of S_2 was approximately equal to that of the N atoms (HCN basis), reaction (7) would have to be faster than

$$N + NS \longrightarrow N_2 + S$$

This behaviour is the reverse of that observed for the analogous oxygen systems, although the heats of reaction of the corresponding reactions are similar. For the oxygen analogs,

$$N + O_2 \longrightarrow NO + O$$

is several orders of magnitude slower than

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

Smith and Jolly (135) made qualitative studies of the reactions of various sulphur compounds with active nitrogen from a microwave discharge, in an attempt to find a useful synthetic method for producing sulphur-nitrogen compounds. The reactions with sulphur compounds containing divalent sulphur (e.g., H_2S, COS) yielded sulphur-nitrogen products. The brief study with COS indicated that $(NS)_x$ was the only nitrogen-containing product. This polymer was identified by its dark blue colour and its conversion to S_4N_4 by hot solvents. On the other hand, the reactions with sulphur compounds containing sulphur atoms with a positive formal charge (e.g., $SOCl_2$, SO_2) did not yield sulphur-nitrogen products. In fact, SO_2 was found to be inert toward atomic nitrogen, and a very high flow rate of SO_2 , of the order 120×10^{-6}mole/sec, was required to extinguish the nitrogen afterglow with an N atom flow rate of only 0.95×10^{-6} mole/sec.

As a result of this study, Smith and Jolly concluded that the formation of sulphur-nitrogen compounds may be associated with a direct attack of the nitrogen atoms on the S atoms in the particular sulphur compound. Atomic nitrogen was assumed to act as an electrophilic reagent for those sulphur compounds that contained more than one pair of lone electrons. The inertness of nitrogen atoms toward SO_2 was explained on the basis that this compound has a positive formal charge, since it possesses only one pair of lone electrons. In the interpretation of their results, Smith and Jolly, did not consider the possibility that reactive species other than atomic nitrogen might be present in the glowing gas.

THE PRESENT PROBLEM

At present, only a few reactions of inorganic substances with active nitrogen appear to be initiated by energy transfer from an excited nitrogen molecule. Ammonia is the classic example in which such a process appears to occur; other probable examples are the reactions of I_2 (63), GeH_4 (136), BCl_3 (136), and TlI (65).

Since a preliminary study of the SO_2-active nitrogen system (cf.ref. 137) revealed a remarkable resemblance to the corresponding ammonia system, the study was extended with a view to obtaining, if possible, a better understanding of the possible energy transfer processes that might be responsible for such reactions. In particular, it was hoped to obtain rate constants for the SO_2 reaction over a wider range of temperature than was possible for the NH_3 reaction, where, it will be recalled, H atom reactions supervened as a disturbing element. Comparative studies with active nitrogen from microwave and condensed electrode discharge systems were also desirable, with attention to the behaviour in "unpoisoned" systems and in systems "poisoned" with various addends to the nitrogen system.

Since the initial products of decomposition of SO_2 were almost certainly SO and O atoms, and SO_3 was readily identified as a final product of the reaction, the corresponding reactions of active nitrogen with SO and SO_3 were also studied independently, to enable their presence during the decomposition of SO_2 to be taken into account in the analysis of the data for the SO_2 reaction. These studies also involved identification of reaction products and evaluation of the rate constants and their temperature dependence, to obtain some insight into the mechanisms of the reactions.

EXPERIMENTAL

MATERIALS

"Bone-dry" nitrogen (Linde, Canada) of 99.7% purity, was used throughout this investigation. Traces of oxygen were removed from it by passing it through a copper furnace maintained at 400-450°C, after which it was passed through liquid nitrogen traps to remove traces of moisture, carbon dioxide, etc.

Argon (Canadian Liquid Air Co.) of 99.99% purity, helium (Air Reduction Canada) of 99.995% purity, oxygen (Canadian Liquid Carbonic) of 99.5% purity, hydrogen (Weldco Canada) of 99.8% purity, and carbon monoxide (Matheson) of 99.5% purity, were all used with no purification other than removal of water vapour in liquid nitrogen traps.

Anhydrous ammonia, and sulphur dioxide (Matheson) of 99.99% purity, were subjected to two bulb-to-bulb distillations during which only the middle fractions were retained.

Carbonyl sulphide (Matheson) of 96% purity, and methane, ethylene, ethane, cyclopropane, propane and n-butane (Matheson, 99.00-99.5% pure) were similarly distilled and stored in 5 litre bulbs at a pressure of about 750 torr.

Nitric oxide (Matheson) of 98.5% purity, was further purified by passing it through a column of 20 mesh silica-gel (Fisher Scientific Co.) at -78°C to remove most of the nitrogen dioxide. This was followed by a trap-to-trap distillation of NO through a silica-gel column, with the final distillation from a trap warmed to -78°C. The NO gas finally collected in the liquid nitrogen trap was a bluish-white solid. It was stored in a 5 litre bulb at about 700 torr.

Sulphur trioxide (Allied Chemicals, Canada) of 99% purity, a volatile liquid at room temperature, was stored in a cylindrical glass ampoule of uniform cross section. This ampoule was surrounded by a large dewar flask filled with water at room temperature, to prevent significant temperature changes in the SO_3 as it evaporated during an experiment (SO_3 has a high heat of vapourization, comparable with that of water). This arrangement permitted flow rates of 20 to 30 x 10^{-6} mole/sec for a period of 100 sec with excellent control. Most of the flow rates used were in the range between 3 x 10^{-6} and 20 x 10^{-6} mole/sec and these could be controlled within 1%.

Sulphur monoxide was obtained from the reaction of COS with oxygen atoms by a procedure that will be described in some detail later. Essentially, the method involved the quantitative reaction of COS with oxygen atoms obtained from the reaction of NO with active nitrogen (138). The reactions involved were $NO + N \rightarrow N_2 + O$ followed by $COS + O \rightarrow SO + CO$. The flow rates of NO and COS were maintained equal throughout an experiment, to produce the equivalent flow rate of SO with which the active nitrogen (main apparatus) then reacted.

APPARATUS

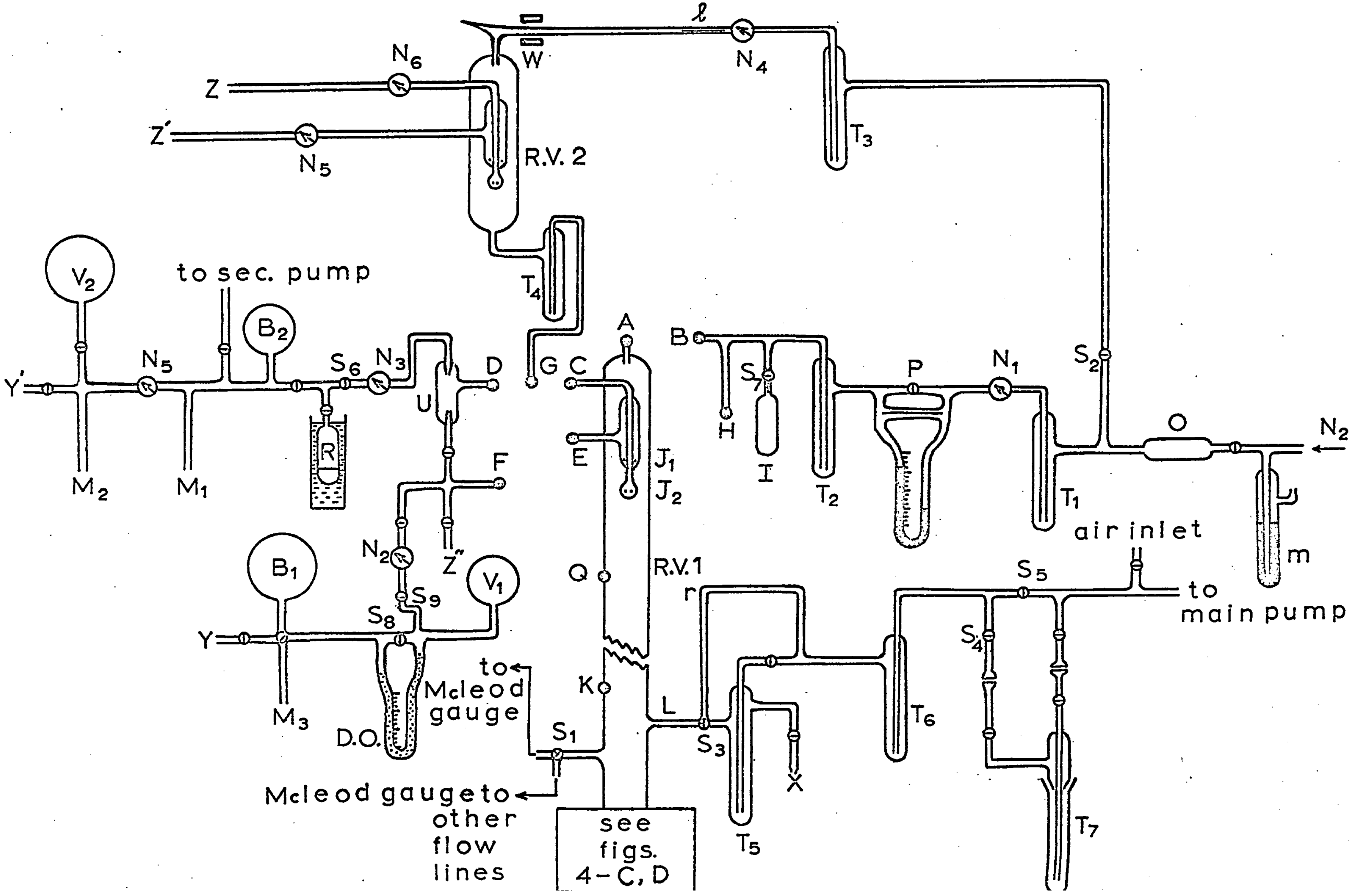
The apparatus used is shown diagramatically in Fig. 3. It was essentially a fast flow system, in which active nitrogen was produced in either a condensed electrode discharge or in a microwave discharge between points A and B. A stream of nitrogen, maintained at a pressure slightly above atomospheric by a manostat m, was passed through a liquid nitrogen trap T_1, and its flow rate controlled and monitored by the needle valve N_1, and the capillary flowmeter P, respectively. With a pressure differential of about 660 torr across the capillary flowmeter a nitrogen pressure of about 2 torr was maintained within the reactor by a Cenco "Hypervac 23" pump (ultimate vacuum 2 microns). This pressure corresponded to a molecular nitrogen flow rate of about 170 x 10^{-6} mole/sec at 27 °C. The pressure in the reaction tube was measured with a tilting McLeod gauge. The gauge could also be connected to other flow lines by the 3-way stopcock S_1, Fig. 3.

The flowmeter for nitrogen gas was operated within the range of 150-400 x 10^{-6} mole/sec and was calibrated in the manner described in detail by Morgan (139). The calibration basically consisted in determining the rate with which a soap film traversed a volume in a gas burette at a pressure of 760 torr of flowing nitrogen. The molecular flow rate was then calculated from the expression

Figure 3

Diagram of the Apparatus

B_1, B_2 - Storage and ballast bulbs, respectively
D.O. - Differential oil manometer
H - Hydrogen inlet
I - Water container
J - Reactant jet
ℓ - Fine capillary
m - Manostat
M - Mercury manometer
N - Needle valve
O - Copper furnace
P - N_2 flowmeter
R - SO_3 ampoule surrounded by water bath
R.V. - 1,2 - Main and accessory reaction vessels, respectively
S - Stopcock
T - Cold trap
U - Mixing chamber
V - Calibrated volume
W - Microwave cavity
X - To demountable product absorber
Y - To corresponding purification system
Z - To corresponding flow line


ℓ
W
N_4
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J_2
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F
M_2
M_1
N_2
Z″
B_1
V_1
S_9
S_8
Y
M_3
D.O.
Q
R.V.1
air inlet
m
S_5
to main pump
r
S_4
to Mcleod gauge
K
L
S_3
T_6
X
S_1
Mcleod gauge to other flow lines
see figs. 4 – C, D
T_5
T_7

$$\text{Flow} = \frac{V}{t}\frac{P}{RT}$$

where V = volume swept in time, t

P = atmospheric pressure

T = ambient temperature

The flow rate thus calculated is approximately proportional to the square of the pressure difference across the capillary flowmeter (Poiseuille flow), and the calibration is virtually unaffected by changes in pressure within the reaction vessel.

Before the nitrogen was drawn into the discharge tube, the gas was passed through a second liquid nitrogen trap T_2, to remove any residual moisture or CO_2 that might have escaped T_1. Trap T_2 also provided a means to eliminate possible contamination of nitrogen by mercury vapour from the flowmeter. Exposed mercury surfaces in other manometers were covered with dibutyl phthalate to prevent evaporation of mercury from these surfaces. When it was desired to make experiments in a "poisoned" system, the nitrogen stream could be "poisoned" with traces of water vapour from container I, or of hydrogen injected at H (Fig. 3). The water vapour was maintained at low flow rates ($\sim 0.07 \times 10^{-6}$ mole/sec) by a capillary stopcock S_7, and an ice bath around container I. Hydrogen flow rates were controlled and monitored by a flow line similar to that used for the introduction of nitric oxide. Flow rates of hydrogen as low as 0.03×10^{-6} mole/sec were effective in "poisoning" the system.

The condensed electrode discharge occurred in a pyrex glass tube (Fig. 4A) 55 cm long, 2.6 cm I.D., fitted with an aluminum electrode at each end. Each cylindrical electrode, 7.5 cm long and 1.5 cm in diameter, was mounted on a tungsten wire (0.2 cm in diameter) that was sealed through the pyrex tube. When glass wool was introduced into the "U" bends* in the discharge tube and the nitrogen feed lines, Q, were connected at each bend on the side away from the corresponding electrode, no aluminum dust was found to accumulate in any part of the reactor or product traps, even after prolonged operation of the discharge unit.

The electrical circuit used to actuate the condensed discharge is shown schematically in Fig. 4B. It is basically a half-wave rectifier, of two 866-A mercury tubes which charged a 4μF capacitor C, to a voltage adequate to cause break-down within the discharge tube. After the discharge is dissipated in a flash between the electrodes, the resistance of the discharge gap falls sharply, and the potential difference between the electrodes decreases until it can no longer support the discharge. It is then quenched until a subsequent potential increase leads to a new discharge. The charging rate, at a specific pressure within the discharge tube, was governed by

---

* Imersion of these bends in water was essential to prevent the glass wool from glowing during activation of the discharge.

the particular resistance - capacitance combination and the setting of the variac in the primary of the H.T. transformer. The pulse rate could be varied from a distinctly discontinuous discharge to a virtually continuous one by lowering the time-constant of the circuit, i.e., by decreasing the resistance value R, from 5000 to 200Ω and the capacitance C, from 4 to 1 μF. With an almost continuous discharge, it was possible to determine the nitrogen atom concentration by an NO titration, (c.f. "Introduction") without difficulty. Although there was no marked difference in the active nitrogen flow rate with a discontinuous and a practically continuous discharge in a "poisoned" system, the "continuous" discharge greatly accelerated the approach to steady conditions in an "unpoisoned" system. It appeared also to give a higher active nitrogen flow rate with "unpoisoned" conditions than did the markedly discontinuous discharge.

The microwave discharge tube consisted of a Vicor tubing, 1.3 cm I.D., 12 cm long, connected to the system between points A and B, Fig. 3. A Raytheon diathermy unit (125W power output at 2450 Mc/sec continuous wave radiation) was coupled to the system by a wave guide. Steady operation of the microwave generator was achieved with a voltage regulator in the input line, with the chassis of the unit well grounded.

The main reaction vessel R.V.1, Fig. 3, was a straight pyrex tube, 2.6 cm I.D. and, for most of the studies, 70 cm long. Two coaxial reactant jets J_1, and J_2, were sealed into it about 12 and 16 cm below the inlet from the discharge tube, respectively. Each consisted of a bulb with six fine holes distributed around its circumference.

The reaction tube was surrounded by an asbestos-insulated nichrome furnace. External mercury thermometers were used to measure the temperatures since exothermic recombination of atomic species and/or de-excitation of excited molecular species on a temperature measuring device in the gas stream may introduce quite large uncertainties in the temperatures recorded. One thermometer was placed at level "zero" (jet J_2, Fig. 3) and a second at a point 60 cm below the first. The upper thermometer generally gave a reading about 15°C higher than that of the lower thermometer at temperatures in the range 200-300°C.

The bottom of the reaction vessel was provided with a coupling R, through which a glass tube (Fig. 4C) could be inserted into the reaction tube. If carefully handled, the tube could be moved under vacuum conditions. For some experiments the tube carried a jet at its upper end, and the lower end was connected by tygon tubing to either an NO or ethylene flow line (F, Fig. 3). This set-up was used particularly for the reaction of SO with active nitrogen, in which different reaction times were obtained by terminating the reaction with NO introduced into the reactor at different distances from the SO inlet. For other experiments, particularly those involving SO_2 as reactant, the tube was fitted with a metal target, as shown in Fig. 4D, which was used to terminate the reaction after different reaction times by moving it to different positions with a friction drive, U. The guide tube, V, prevented the target from touching the wall as it was moved in the reaction vessel. The friction drive consisted simply of a rubber sleeve, R, that pressed against the movable tube through a slot in the guide tube V.

The circular target, about 0.2 cm smaller in diameter than the reaction tube, was made from 45 mesh platinum gauze. It was electroplated first with copper and then with cobalt, as outlined in Modern Electroplating (140) employing a simple series voltage source electrical circuit.

The target technique could not be used to terminate the reaction of active nitrogen with SO_3, since SO_3 attacked the cobalt and quickly rendered the target ineffective. The reaction was, therefore, stopped by a low temperature trapping method, since SO_3 has a relatively high freezing point. The trap consisted of a U-tube joined to the bottom of the reaction vessel, which increased the effective overall length of the

Caption of Figure 4

A: The Condensed Discharge Tube

- A - Tungsten wire
- E - Aluminum electrode
- P - Outlet (connected to A, Fig. 3)
- Q - N_2 feed line (connected to B, Fig. 3)
- U - "U" - bends

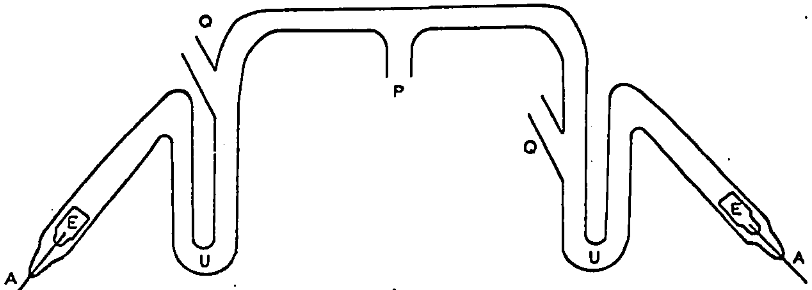
B: The Electrical Circuit of the Condensed Discharge

C: The Movable Reactant Jet Assembly

- G - Tygon tubing (connected to F, Fig. 3)
- J - Jet
- R - Metal coupling

D: The Movable Metal Target Assembly

- B - Brass holder
- L - Movable tube
- R - Rubber sleeve
- T - Circular target
- U - Friction drive
- V - Fixed guide tube


Q
P
Q
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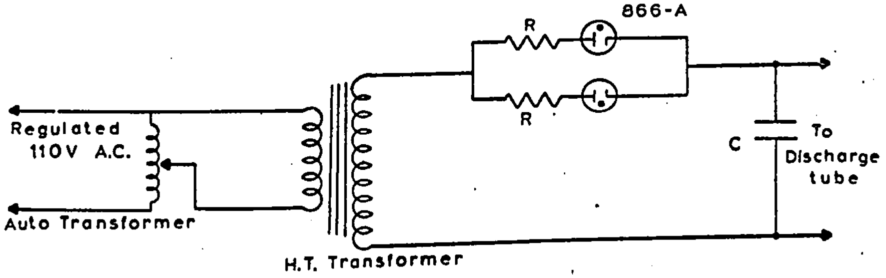
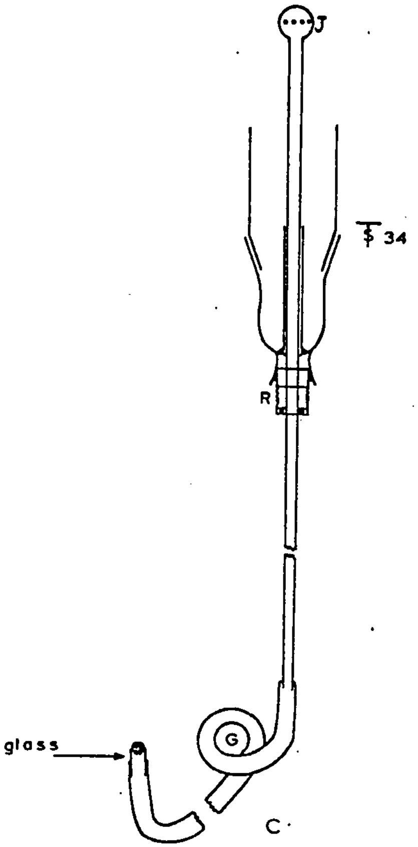
A


R
866-A
R
Regulated
110V A.C.
Auto Transformer
H.T. Transformer
C
To
Discharge
tube

B


J
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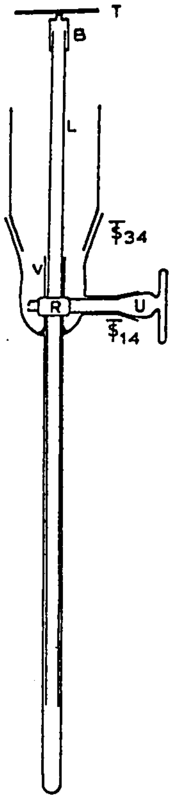
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₮14

D

reactor to 90 cm. The U-tube was immersed in a suitable dewar flask, into which liquid nitrogen was then introduced and carefully maintained at a constant level.

Sulphur dioxide, ammonia and hydrocarbons were introduced, as desired, through jet, J_2, and the flow controlled by needle valve, N_3. The flow lines were of the type shown in Fig. 3. Each consisted of a known volume, V_2, a smaller ballast volume, B_2, two mercury manometers M_1, M_2, and two needle valves, N_3, and N_5. Needle valve, N_3, which served as a variable capillary was set to a desired position and stopcock S_6 turned on at the beginning of an experiment. After the reaction was started, care was taken to maintain a constant pressure within the ballast volume by manipulating needle valve N_5. The average flow rate of the reactants was determined by measuring the pressure difference in the known volume before and after the reaction. The flow rates measured in this way were compared with those obtained from chemical analysis of the easily trapped gases (NH_3, SO_2, SO_3). Agreement was within 1 to 2%.

The flow of nitric oxide from bulb B_1, Fig. 3, was controlled and monitored by the needle valve N_2, and the oil manometer D.O., respectively, after which it entered the reaction vessel through either jet J_1, (E and F connected, Fig. 3), or through the movable jet J, Fig. 4C.

Nitric oxide flow rates were within a range of 0.3 to 25 x 10^{-6} mole/sec. A flow line similar to the one described for the introduction of NH_3 or SO_2 was used for the flow rate range 5 to 25 x 10^{-6} mole/sec. For flow rates less than 5 x 10^{-6} mole/sec, a differential oil manometer (D.O., Fig. 3) was used to overcome the inconveniently long response times that accompanied the use of a mercury manometer. Stopcocks S_8 and S_9 were normally open during an experiment. To determine the flow rate, stopcock S_8 was closed, and the rate of differential pressure drop between storage bulb, B_1, and the calibrated volume V_1, was measured on the oil manometer. This method was sufficiently sensitive and accurate. The error involved in the measurement of these flow rates did not exceed 1%. The flow rate was calculated with the expression

$$\text{Flow} = \frac{P}{t} \frac{V_1}{RT}$$

where P/t = rate of differential pressure drop

V_1 = calibrated volume of bulb and accessory tubing

T = ambient temperature

The same method was applied to the higher flow rate range by using a sufficiently long oil manometer and limiting the time of operation to less than 10 sec, so that the pressure drop in the storage bulb was not excessive. In this range, the use of mercury and oil manometers gave data that agreed within 1%.

Sulphur monoxide was generated at 225°C in an auxilliary reaction vessel, R.V.2, Fig. 3. Molecular nitrogen that had passed through stopcock S_2, liquid nitrogen trap T_3, and the flow control system consisting of the needle valve N_4, and associated glass capillary ℓ, was partially dissociated by the microwave cavity W, to yield active nitrogen. Nitric oxide from a secondary flow line, controlled and monitored by needle valve N_5, and a differential oil manometer (not shown), was allowed to react with the active nitrogen to yield an equivalent flow of oxygen atoms. Carbonyl sulphide was then added through a similar flow line, controlled by needle valve N_6, to the oxygen atom stream. The reaction of carbonyl sulphide with oxygen atoms did not seem to occur appreciably at room temperature, since the effluent from an unheated vessel appeared to contain only unreacted carbonyl sulphide. When the unheated effluent was introduced into an active nitrogen stream in the main reaction vessel, it seemed merely to weaken the yellow afterglow. However, when the carbonyl sulphide-oxygen atom mixture was passed through a heated (225°C) generator, the products of the reaction completely quenched the active nitrogen glow in the main reaction tube. When the products of the COS + O reaction were passed through a liquid nitrogen trap T_4, SO condensed to a yellow-orange solid (141). The solid lost its colour when the trap was warmed to room temperature, and only a faint yellow deposit remained on the wall. The yellow deposit was not analyzed but was almost certainly sulphur, a product of the rearrangement of SO above -80°C (142). As with a film of sulphur (143,144), the deposit could be removed completely by prolonged passage of active nitrogen or atomic oxygen through the system. Sulphur dioxide was also identified as a product of the rearrangement, and no unreacted carbonyl sulphide remained. The disproportionation of SO is known to occur by the reaction $2SO \rightarrow S + SO_2$. After its generation, as above, sulphur monoxide was introduced into the main reaction vessel through jet J_2, (C and G connected, Fig. 3), to react with active nitrogen from a microwave discharge.

In the studies with sulphur trioxide, the reactant entered the main reaction vessel either through jet J_2 (C and D connected, Fig. 3), or for measurement of rate constants, through two other jets located in the reaction tube at Q and K, 30 and 60 cm below J_2, respectively. The flow of SO_3 was controlled by needle valve, N_3. The flow rates of active nitrogen could be measured at all these levels in the reaction vessel by the NO titration.

Condensable gases were removed from the gas stream by two large liquid nitrogen traps, T_5 and T_6. Both these traps could be isolated from the system and from the pump by manipulating stopcocks S_3, S_4 and S_5, to allow distillation of the reaction products into a small demountable trap attached at X, Fig. 3. The trap T_5, could be by-passed when necessary (r, Fig. 3). During SO_3 reactions, condensable products were first trapped in T_5 and T_6, which were then isolated from the reaction vessel by stopcock S_3. When the traps were warmed to room temperature, the products were distilled into a demountable evacuated trap immersed in liquid nitrogen, and into which outgassed, distilled water had been previously introduced. It was essential to adopt this procedure, since excess SO_3, when condensed, occluded non-condensable gases within its crystals; these gases were released when the crystals melted and hindered the diffusion of the products and hence their distillation.

SOME FEATURES OF THE FLOW SYSTEM

During measurements of rate constants, either a movable reactant jet, or a movable cobalt target was placed at a desired level in the reactor to quench the reaction. The distance from either one to the fixed reactant inlet jet determined the reaction time for a particular molecular nitrogen flow rate and pressure within the reactor. However, it should be noted that for reactions at constant pressure the reaction time depends upon the extent to which the volume changes during the progress of the reactions. The reactions that were investigated in this study were not associated with a change in the number of moles, except, perhaps, for some 3rd order recombination process the effect of which was too small to cause an appreciable change in the total volume flow rate.

Another point of interest arises from the fact, that in laminar flow there is always some radial variation of velocity. With the present flow system, in which laminar flow was conceivable (Reynold's number ranging within 18-55), and longitudinal mixing was not excessive, this would result in a radial diffusion of reactants and products in opposite directions. However, if there is no mechanical mixing, the concentration at any point within the reactor will attain a steady state concentration independent of time. In fact, the concentration at any point, ℓ , within the reaction vessel will equal the concentration in a static system of the same volume that has reacted for a time t, equal to $t = \ell/V$ (where V linear velocity of the gas).

EXPERIMENTAL PROCEDURE

The apparatus was normally kept under vacuum. Before each experiment, it was evacuated to about 2 microns, after which nitrogen was admitted to the system for 5 to 10 minutes, to establish steady state pressure within the reactor. For reaction temperatures above room temperature, the furnace around the reaction vessel was turned on for 30 to 45 minutes, to establish thermal equilibrium before a reaction was started. The condensed discharge was activated for at least one hour in the "poisoned" system, and for 2 to 3 hours in the "unpoisoned" system, prior to every reaction. However, the microwave discharge had to operate for only 10 minutes before an experiment, in either type of system, to allow the active nitrogen flow rate to attain a steady value.

Reactions were initiated by admitting the reactant through the appropriate jet, and terminated by stopping the flow of the reactant. The discharge was then stopped, and the traps, T_5 and T_6 isolated from both reaction vessel and the pump. Distillation of the trapped reaction products was then begun. Experiments were usually made with a range of reactant flow rates, and over a range of reaction times and temperatures. When it was desired to allow the reaction to proceed to completion, either the movable NO jet, or the cobalt target, as the case required, was placed below the exit tube leading to the trap (L, Fig. 3). Duration of the experiments was determined by the time necessary to collect sufficient quantities of products for subsequent satisfactory analysis, but was generally from 100 to 200 sec.

Analysis of reaction products

Hydrogen cyanide, produced in the active nitrogen reactions with the various hydrocarbons, in the absence or presence of NH_3 or SO_2, was analyzed argentometrically as outlined in the Leibig-Deniges method (145). The gas trapped in T_5 and T_6 was slowly sublimed into a movable alkaline absorber, attached at X, Fig. 3. To ensure slow sublimation, and thereby minimize polymerization of the HCN, the absorber was removed from the liquid nitrogen trap and immersed in carbon tetrachloride to obtain a coating of solid carbon tetrachloride on the outside, which maintained the temperature at about -24°C.

Ammonia was analyzed by the familiar Kjeldahal distillation, using 0.02 N solutions of acid and base.

Sulphur dioxide was determined by iodimetry. The gas was allowed to distill from the low temperature trap into a small demountable absorber that contained about 50 ml of distilled water, previously outgassed and frozen in liquid nitrogen. This trap was then removed and warmed, and the solution titrated with 0.02N iodine standard solution to thyodene endpoint. Sulphur dioxide formed in the reaction of either active nitrogen or oxygen atoms with SO_3 was qualitatively identified with sodium nitroprusside and estimated quantitatively by an iodine titration.

Sulphur trioxide was estimated by acid-base titrations. It was essential to agitate its aqueous solutions to bring about complete solution. Blank experiments with a standard iodine titration showed that some reducing agent was present in the trapped products after SO_3 had passed through freshly greased stopcocks, presumably as a result of a slow reaction of the gas with the grease. The reducing agent reached a constant level after three or four such experiments had been made.

Other reaction products were identified either by standard chemical procedures or by an infrared Perkin-Elmer 337 grating spectrophotometer. Infrared spectra were taken for samples in solution or deposited on NaBr pellets.

RESULTS

I. EFFECT OF TIME ON ACTIVE NITROGEN FLOW RATE

A previous study in this laboratory (146) indicated that active nitrogen flow rates in an "unpoisoned" discontinuous condensed discharge attained a steady value only after prolonged operation of the discharge unit. It was of more than passing interest, at the outset, to determine whether these observations were relevant to the present system and to extend the investigation to "poisoned" systems, since such studies would help to define the operating conditions most conducive to reproducible results.

The results reported in Table I and Fig. 5 were obtained for an "unpoisoned" discontinuous condensed discharge at 2 torr,

TABLE I

Nitric Oxide Titration as a Function of Time

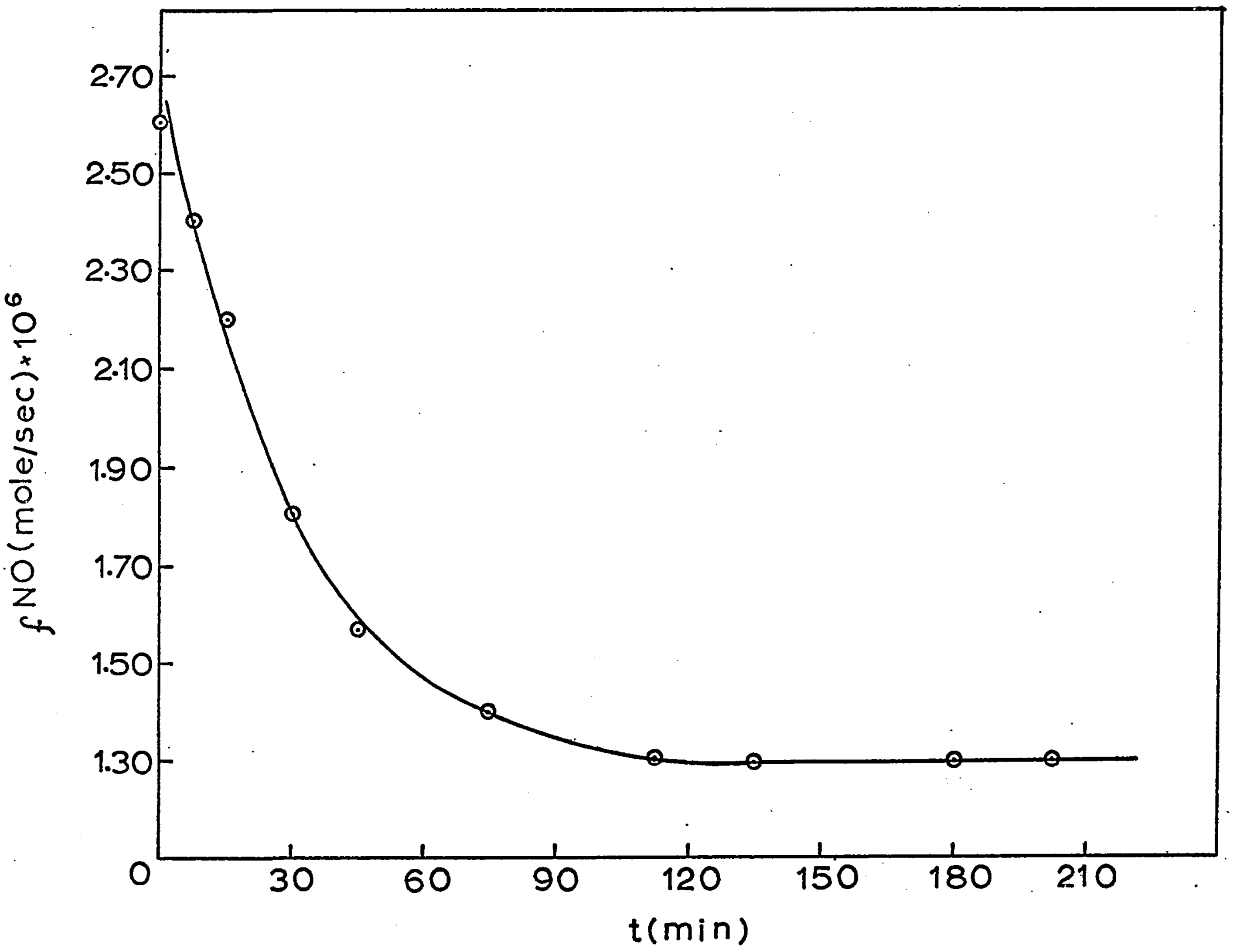
Condensed discharge - "unpoisoned" system

t (min)	NO* (mole/sec) x 10^6
0	2.62
7	2.43
15	2.20
30	1.80
45	1.55
75	1.40
112	1.35
135	1.35
180	1.30
202	1.30

* Reproducible within ±2%.

Figure 5

NO Titration as a Function of Time
("unpoisoned" system)
Molecular nitrogen flow rate 160 x 10^{-6} mole/sec
(Total pressure 2 torr)



2·70
2·50
2·30
2·10
1·90
1·70
1·50
1·30
f NO (mole/sec)×10^6
0
30
60
90
120
150
180
210
t(min)

with nitric oxide estimation of the prevailing average active nitrogen flow rate. Data showing similar behaviour were obtained for total pressures of 2.5 to 3.5 torr. It seemed safe to assume that a lapse of 2 to 2 1/2 hours would be required, in this type of system, to reach constant active nitrogen flow rates.

Similar experiments in an "unpoisoned" system, with a microwave discharge, gave different results. For these conditions only about 10 minutes were required for the active nitrogen to attain a steady flow rate. Its value was then comparable with that finally attained in an "unpoisoned" condensed discharge system.

When water vapour, at about 5 x 10^{-6} mole/sec, was admitted to the molecular nitrogen before it entered a discontinuous condensed discharge, the NO titration attained a constant value within 30 minutes of operation. The corresponding active nitrogen flow rate was about 18 times that in an "unpoisoned" system, and its afterglow was an intense golden-yellow. With a relatively smaller amount (0.1 x 10^{-6} mole/sec) of water vapour through the discharge, the active nitrogen flow rate decreased after 30 minutes to a steady value about 10 times that in an "unpoisoned" system. However, when the water vapour flow rate was changed from 5 x 10^{-6} to 0.1 x 10^{-6} mole/sec, without interrupting the discharge, the decrease in active nitrogen flow rate from one level to the other required 3 hours of operation. The results are given in Table II.

TABLE II

Nitric Oxide Titration as a Function of Time

Condensed discharge - system "poisoned" with H_2O vapour
(H_2O flow changed from 5×10^{-6} to 0.1×10^{-6} mole/sec at t = o)

t (min)	NO (mole/sec) $\times 10^6$
0	23.5
60	22.3
83	21.2
90	20.0
105	18.0
142	14.5
170	13.2
200	13.2
240	13.2

Similar results were obtained by using hydrogen as a "poison". One hour of condensed discharge operation (discontinuous or pulsating discharge*) and relatively lower hydrogen flow rates could be employed to attain constant active nitrogen flow rates comparable to those observed in a system "poisoned" with water vapour. These results are reported in Table III and Fig. 6 together with related data from a virtually continuous ("pseudo-continuous") condensed discharge "poisoned" with hydrogen (0.07×10^{-6} mole/sec) for which 7 to 8 hours were

---

* In a "pseudo-continuous" condensed discharge "poisoned" with a trace of H_2 the NO titration attained a steady value within 5 minutes.

needed to restore "unpoisoned" conditions when the hydrogen flow was stopped*.

TABLE III

Nitric Oxide Titration as a Function of Time

System "poisoned" with hydrogen

a. Discontinuous condensed discharge

t (min)	NO (mole/sec) x 10^6
0	16.3
7	15.0
22	14.4
32	13.6
45	13.3
75	13.3
120	13.3

b. "Pseudo-continuous" condensed discharge (H_2 flow stopped

t (min)	NO (mole/sec) x 10^6
0	21.0
30	15.3
60	14.0
90	13.3
120	13.3
150	13.3
360	12.6
390	11.0
420	7.2
450	5.3
480	3.00

---

* Prolonged periods of operation (8 to 10 hours) were needed to restore "unpoisoned" conditions with a previously "poisoned" pulsating condensed discharge.

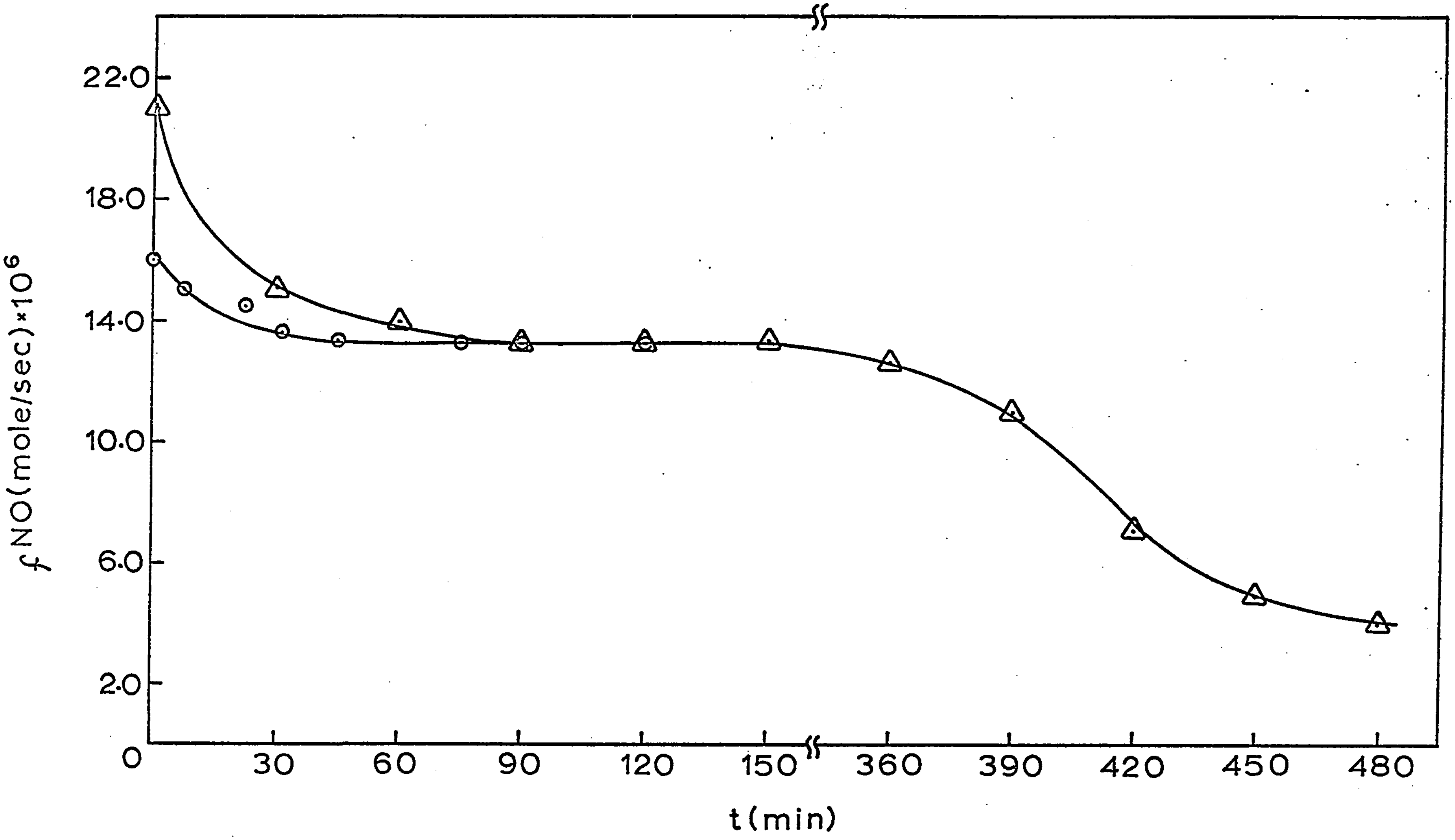
<u>Figure 6</u>

NO titration as a Function of Time

System "poisoned" with hydrogen (0.07 x 10^{-6} mole/sec)
Total pressure 2 Torr

O - Discontinuous condensed discharge

△ - "Pseudo-continuous" condensed discharge - (H_2 flow stoppe


22·0
18·0
14·0
10·0
6·0
2·0
0
f_{NO}(mole/sec)×10^6
30
60
90
120
150
360
390
420
450
480
t(min)

No significant changes were noticed in the NO titration endpoint when hydrogen was substituted for water vapour in a microwave discharge. The active nitrogen flow rate in this system was only slightly increased (15%) and attained a steady value within about 10 minutes. "Unpoisoned" conditions could be established within about 10 to 15 minutes after the flow of H_2O vapour or H_2 was stopped.

Although nitric oxide was chosen to estimate the prevailing active nitrogen concentrations throughout this study, some measurements with ethylene were also made. The condensed electrode discharge system, whether "poisoned" or "unpoisoned", always exhibited a lower active nitrogen concentration inferred from the HCN production than it did from the NO titration. Representative data are shown in Table IV with an NO/HCN ratio between 1.1 and 1.8. It is interesting, perhaps that the one experiment with an increased surface-to-volume ratio in the reaction zone appeared to favour an NO/HCN ratio closer to unity. This behaviour might merit further study.

TABLE IV

NO - HCN Estimates of Active Nitrogen Concentration

(Condensed discharge)

Level in reactor	NO (mole/sec) x 10^6	HCN (mole/sec) x 10^6	NO/HCN**
a. "Unpoisoned" system			
J_1*	2.35	2.10	1.10
J_1	1.83	1.20	1.52
65 cm below J_1	0.360	0.200	1.80
b. "Poisoned" system			
J_1	20.0	14.0	1.43
J_1	21.0	15.0	1.40
65 cm below J_1	8.6	5.5	1.56

* Surface-to-volume ratio increased within the reaction zone.

** Within ±3%.

II. REACTIONS OF SULPHUR DIOXIDE WITH ACTIVE NITROGEN

(1) COMPARISON OF NH_3 AND SO_2 REACTIONS

Blank experiments showed that the efficiency with which either NH_3 or SO_2 was trapped in the liquid nitrogen traps, T_5 and T_6, was very high. This was probably due to the decrease in the linear velocity of the gas that occurred as it entered these wide-bore traps. The increase in efficiency with an additional trap was practically insignificant.

Experiments were first made in an "unpoisoned" system, using either a condensed electrode or a microwave discharge unit to form the active nitrogen. Prevailing active nitrogen flow rates, estimated by nitric oxide, were 2.35 and 1.80 x 10^{-6} mole/sec, respectively. With these flow rates of active nitrogen, practically no destruction of either NH_3 or SO_2 was detectable. Neither was an NO titration altered down stream when SO_2 was introduced, at various flow rates, 20 or 40 cm upstream in a microwave discharge system. These results are given in Table V. With these conditions an intensification of the yellow afterglow occurred when the flow rate of SO_2 exceeded about 0.5 x 10^{-6} mole/sec, and remained practically unaltered for higher flow rates.

Since it was virtually impossible to detect any decomposition of either NH_3 or SO_2 at the active nitrogen, obtained in an "unpoisoned" system, experiments were made with the higher active nitrogen concentrations attainable in a "poisoned" system.

TABLE V

Reaction of Sulphur Dioxide with Active Nitrogen

Microwave discharge - "unpoisoned" system
N_2 flow rate 180 x 10^{-6} mole/sec
Total pressure 2 torr

SO_2 input (mole/sec) x 10^6	NO titration - SO_2 added (mole/sec) x 10^6
Reaction time* 60 msec; NO titration (No SO_2 added) = 1.30 x 10^{-6} mole/sec	
0.35	1.30
0.50	1.30
0.90	1.30
1.9	1.30
4.0	1.30
Reaction time 120 msec; NO titration (No SO_2 added) = 0.80 x 10^{-6} mole/sec	
0.35	0.80
0.50	0.80
0.90	0.80
1.9	0.80
4.0	0.80

* Standard error within ±5%.
NO and SO_2 flow rates reproducible within ±2 - 3%.

When a relatively large amount of water vapour (~5 x 10^{-6} mole/sec) was admitted to a microwave discharge system, the active nitrogen flow rate was increased only slightly (15%) and neither NH_3 nor SO_2 was detectably decomposed. Neither was any destruction of NH_3 or SO_2 observed when the configuration of the microwave discharge tube had been altered to produce a relatively higher active nitrogen content in a "poisoned" system (Table VI).

TABLE VI

Reaction of Sulphur Dioxide with Active Nitrogen

Microwave discharge* - "poisoned" system
N_2 flow rate 180 x 10^{-6} mole/sec
Total pressure 2 torr
(Reaction time 430 msec)

NO titration** (mole/sec) x 10^6	SO_2 input (mole/sec) x 10^6	SO_2 recovered (mole/sec) x 10^6
5.0	8.0	8.2
5.0	10.4	10.6
5.7	5.4	5.6
5.7	8.0	7.8
5.7	12.5	12.6

* Configuration of discharge tube altered.
**Active nitrogen flow rate estimated at SO_2 inlet.

With a similar amount of water vapour through a condensed discharge, the active nitrogen flow rate, estimated by NO, was increased to 21 x 10^{-6} mole/sec, and the SO_2 reaction was accompanied by a blue glow which extended from the SO_2 inlet to the cold trap***. The amount of SO_2 decomposed increased markedly with SO_2 input (Table VII) and a pale yellow solid was collected in the cold trap. When this was warmed to room temperature, an oily film appeared, although some whitish-yellow solid still remained. The oily residue was acidic and was probably sulphuric acid. The solid residue was probably formed, in part at least, as a product of the reaction of SO_2 with NO_2 during the initial surge of nitric oxide in the NO titration. Similarly, an apparently continuous increase in the amount of NH_3 decomposed with NH_3

***Efforts to reproduce the blue emission at lower active nitrogen flow rates were unsuccessful.

flow rate (Table VII) was due mainly to formation of a product that liberated NH_3 when it was treated with alkali. This solid was probably ammonium nitrite and/or nitrate salt. Consequently, after an NO titration, the cold traps were warmed to room temperature to remove NO and NO_2 residuals before either NH_3 or SO_2 was introduced into the system.

TABLE VII

Reactions of SO_2 and NH_3 with Active Nitrogen

Condensed discharge - system "poisoned" with H_2O vapour
N_2 flow rate 190 x 10^{-6} mole/sec
NO titration 21 x 10^{-6} mole/sec
Total pressure 2 torr

SO_2 input (mole/sec) x 10^6	SO_2 reacted (mole/sec) x 10^6	NH_3 input (mole/sec) x 10^6	NH_3 reacted (mole/sec) x 10^6
9.0	7.5	3.8	3.8
9.5	9.0	3.9	4.0
14.0	12.3	5.5	5.2
17	13.6	11.3	5.5
47	16.2	14.0	7.0

When the water vapour flow rate was reduced to 0.07 x 10^{-6} mole/sec, with a concomitant decrease in the active nitrogen concentration, the decomposition of SO_2 was not accompanied by the blue glow. Almost no yellow solid was collected, but an acidic oily film was still present in the product trap. The data are shown in Table VIII, together with corresponding results for the NH_3 reaction under the same experimental conditions. (A blank experiment in the absence of NH_3 indicated that no ammonia was formed by reaction of active nitrogen with the trace of H_2O present.)

TABLE VIII

Reactions of SO_2 and NH_3 with Active Nitrogen

Condensed discharge - system "poisoned" with H_2O vapour (0.07×10^{-6} mole/sec)
Total pressure 2 torr

NO titration (mole/sec) x 10^6	SO_2 input* (mole/sec) x 10^6	SO_2 reacted (mole/sec) x 10^6	NH_3 input* (mole/sec) x 10^6	NH_3 reacted (mole/sec) x 10^6
5.0	4.80	1.45	5.05	1.50
5.8	6.03	1.50	6.00	1.53
6.4	6.53	1.50	6.71	1.51
8.0	-	-	10.40	1.50
10.5	9.30	1.90	7.50	1.70
10.5	11.00	1.70	15.60	1.6
13.5	-	-	5.60	2.50
13.5	-	-	8.00	2.20
13.5	-	-	21.0	2.4
21.0	20.0	1.9	-	-
21.0	23.2	2.0	-	-

* Reproducibility within ±1%, corresponding standard error in reacted NH_3 or SO_2 within ±4 - 10%.

The formation of the acidic film and the solid product were almost completely suppressed when the system was "poisoned" with a small amount of hydrogen (~0.03 x 10^{-6} mole/sec) instead of water vapour. The hydrogen was introduced into the nitrogen stream before it entered the discharge. The resulting active nitrogen flow rates were then 13.3 x 10^{-6} and 2.4 x 10^{-6} mole/sec from the condensed and microwave discharges, respectively. These results are shown in Table IX. Also included in the table are data for the corresponding NH_3 reaction. Comparison of the results of the last two tables indicates relatively larger extents of SO_2 and NH_3 reactions in the system "poisoned" with water vapour, compared with the system "poisoned" with hydrogen. This might be ascribed, perhaps, to a change in the characteristics of the discharge due to oxygen atoms or OH radicals.

(2) REACTIONS OF NO AND HYDROCARBONS IN THE PRESENCE OF NH_3 AND SO_2

It is evident from previous data that ammonia or sulphur dioxide were decomposed to approximately the same extent by active nitrogen from a condensed discharge. This suggested that the same species in active nitrogen might be responsible for these two reactions. Since the rate constant for the ammonia reaction had been measured (131), an attempt was made, at this point, to obtain that for the SO_2 reaction by studying the relative amounts of NH_3 and SO_2 decomposed in mixtures of the two. Such attempts were unsuccessful, however, owing to a rapid gas-phase reaction to form a yellow-brown water soluble solid. This reaction also occurred at considerable rate even at a low temperature; the coloured solid was

TABLE IX*

Reactions of SO_2 and NH_3 with Active Nitrogen

Condensed discharge - system "poisoned" with hydrogen ($\sim 0.03 \times 10^{-6}$ mole/sec)
N_2 flow rate 190×10^{-6} mole/sec
NO titration 13.3×10^{-6} mole/sec
Total pressure 2 torr

SO_2 input (mole/sec) x 10^6	SO_2 reacted (mole/sec) x 10^6	NH_3 input (mole/sec) x 10^6	NH_3 reacted (mole/sec) x 10^6
5.60	1.20	6.00	1.20
6.80	1.30	9.30	1.10
8.00	1.10	11.30	1.10
10.20	0.90	14.7	1.3
10.40	1.10	16.2	1.3
11.30	1.60	18.4	1.1
18.9	1.5	20.0	1.2

* Estimated precision and error as in Table VIII.

formed instantaneously when SO_2 was allowed to pass over frozen NH_3 in a liquid nitrogen trap. This solid was probably $(NH_4)_2$-S_2O_5 (147) or $H_2NSO_2NH_4$ (148), which may be formed under anhydrous conditions.

It was then decided to investigate further the possible similarity between the NH_3 and SO_2 reactions by studying the relative effects of NH_3 and SO_2 in the reactions of active nitrogen with various substances (mainly hydrocarbons). It was hoped, by such studies, to gain further insight into the possible role of excited nitrogen molecules in promoting the SO_2 reaction, on the assumption (see "Introduction") that NH_3 was able to inhibit some hydrocarbon reactions by virtue of its ability to remove excited nitrogen molecules that might serve to initiate such reactions.

For the study of these reactions a mixing chamber (U, Fig. 3), of 50 ml capacity, was installed in the appropriate flow lines, to ensure premixing of the reactants before they entered the reaction vessel through a common jet, J_1. The active nitrogen was generated with a condensed discharge, in a system "poisoned" with a trace of water vapour.

(a) The nitric oxide reaction

During this comparative study, either the NH_3 or SO_2 flow rate was continuously varied, while the nitric oxide flow rate was concurrently monitored to complete consumption of nitrogen atoms. Each experiment was of 100 to 120 sec duration during which no solid product was formed (nitric oxide flow rates were never allowed to exceed the active nitrogen flow rate, to minimize possible side reactions). It is evident from the data reported in Table X and Fig. 7 that the NO titration value decreased continuously in the presence of NH_3, while in the presence of SO_2 it was practically constant, up to 70 x 10^{-6} mole/sec of either gas. It might be noted, however, that the results for the higher flow rates were perhaps somewhat influenced by a concomitant increase (~20%) in the total pressure.

TABLE X

Reaction of NO with Active Nitrogen in the Presence of NH_3 and SO_2

N_2 flow rate 190 x 10^{-6} mole/sec
Total pressure ~2 torr
(All values reproducible within ±3%)

NH_3 input (mole/sec) x 10^6	NO titration (mole/sec) x 10^6	SO_2 input (mole/sec) x 10^6	NO titration (mole/sec) x 10^6
0.0	15.7	0.0	15.7
6.2	14.5	2.0	15.7
24.4	13.3	6.2	15.7
46	13.3	28.3	15.7
50	12.1	49	15.7
78	11.7	68	15.7
134	11.7	97	14.5
180	11.7	123	13.3
-	-	136	13.3
-	-	151	13.3

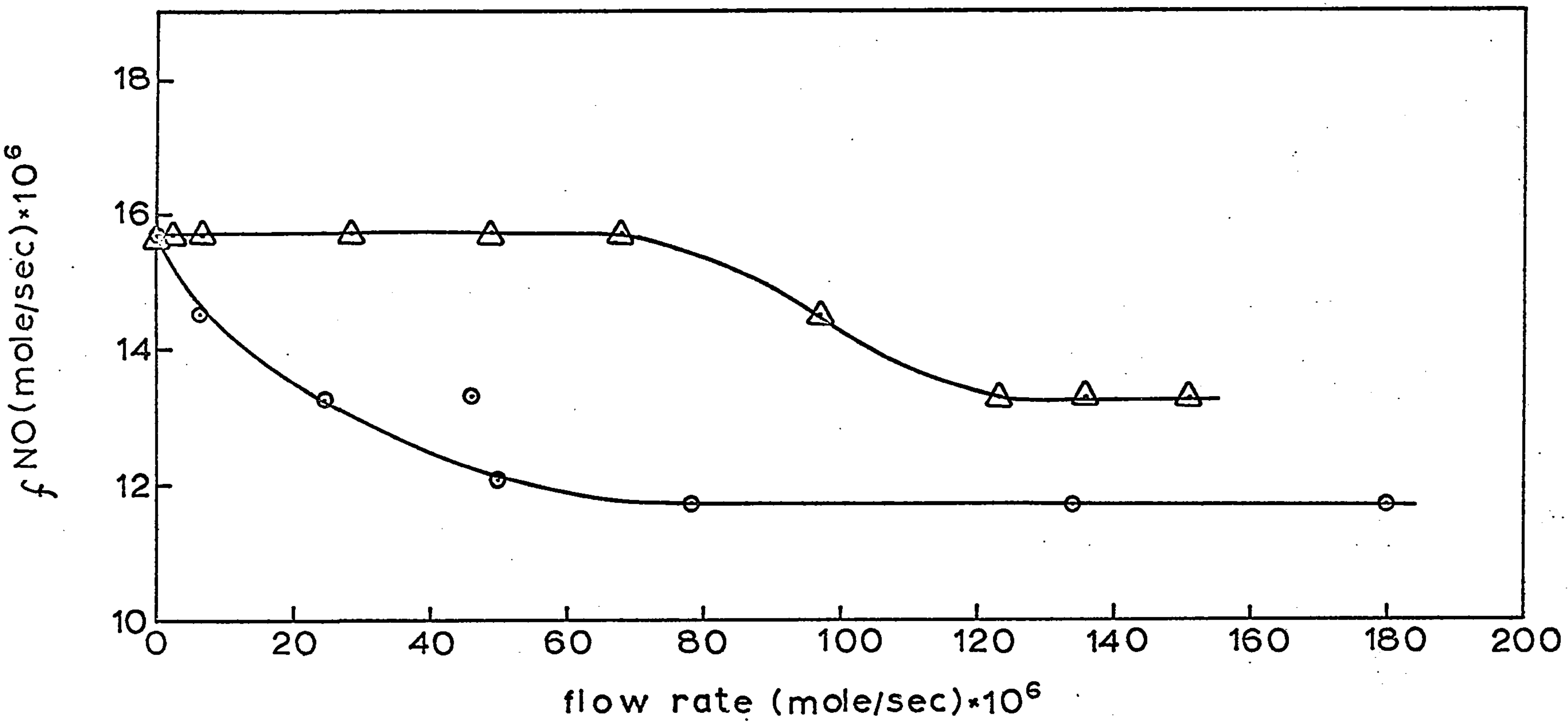
Figure 7

Reaction of Nitric Oxide with Active Nitrogen

NO titration as a function of NH_3 and SO_2 flow rates

○ - In the presence of NH_3

△ - In the presence of SO_2



f NO (mole/sec)×10^6
10
12
14
16
18
0
20
40
60
80
100
120
140
160
180
200
flow rate (mole/sec)×10^6

(b) The ethylene reaction

For this reaction, and for the related reactions of methane and cyclopropane, the flow rate of NH_3 or SO_2 was varied, while the hydrocarbon flow rate was maintained constant, at a value that corresponded to maximum HCN yield (plateau value) in the absence of added NH_3 or SO_2.

With ethylene as reactant, the maximum yield of HCN, in the absence of NH_3 or SO_2, was about 9.5×10^{-6} mole/sec and was attained at ethylene flow rates above 30×10^{-6} mole/sec (the corresponding active nitrogen flow rate inferred from the NO titration was 15.7×10^{-6} mole/sec, so that the NO/HCN ratio for this system was 1.65). The reaction was accompanied by the CN emission, and this persisted in the presence of relatively high ammonia or sulphur dioxide flow rates. The yield of HCN was substantially reduced with low flow rates of NH_3 (Table XI, Fig. 8), but increased above the value in the absence of NH_3 when ammonia flow rates were in excess of about 6×10^{-6} mole/sec. Since back diffusion of ethylene, at these rather high flow rates, could have led to the observed enhancement in HCN production, experiments were made in which the flow of ammonia was replaced by an equivalent flow of molecular nitrogen. No significant change in the HCN yield was observed, even for additional molecular nitrogen flow rates in excess of the largest ammonia flow rates used. In other experiments, nitric oxide was first admitted to the active nitrogen stream to the "titration" endpoint, after which increasing flow rates of nitrogen were added with the NO.

TABLE XI

Reaction of Ethylene with Active Nitrogen in the Presence of NH_3 and SO_2

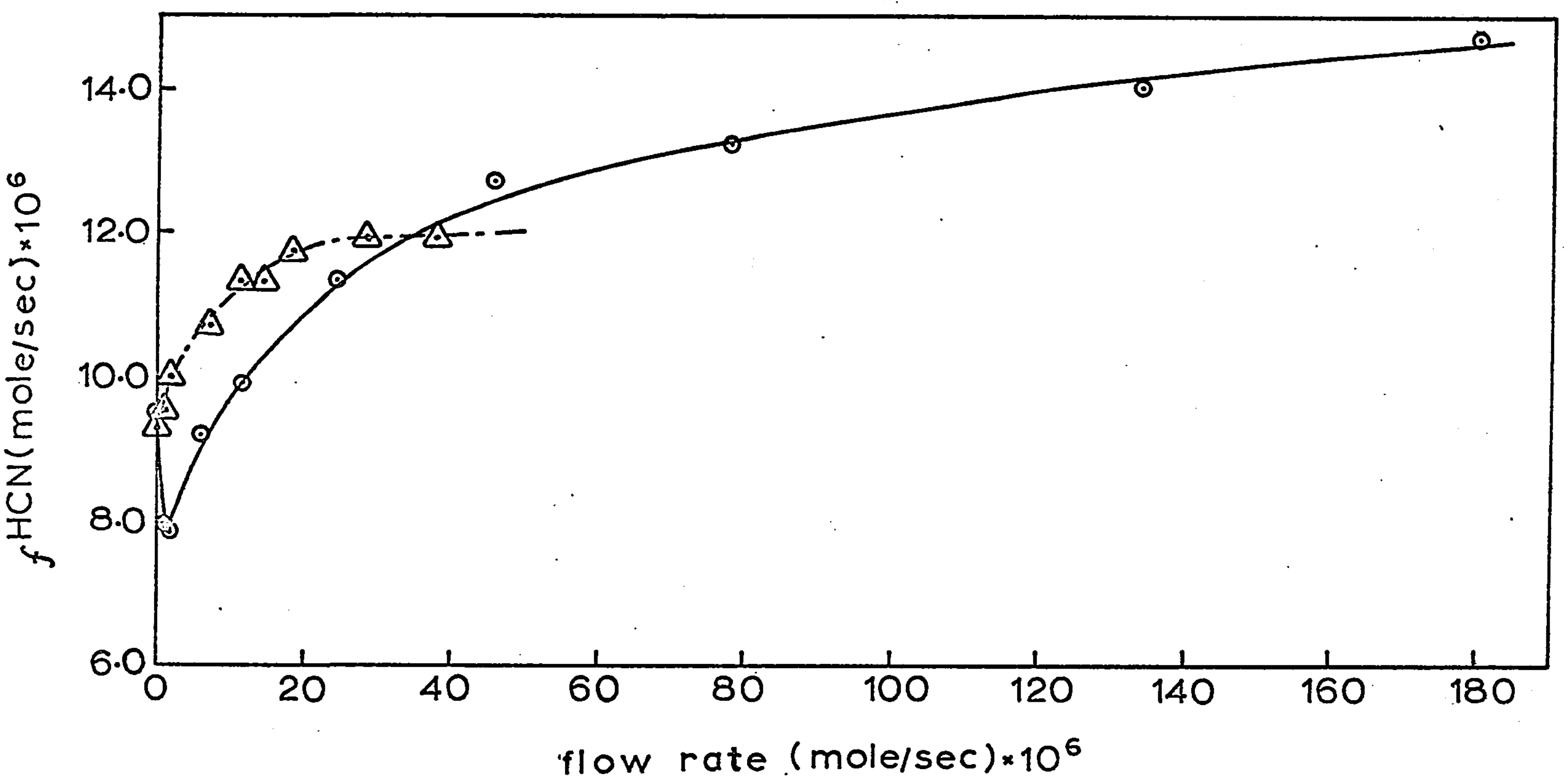
Ethylene flow rates 39 x 10^{-6} and 37 x 10^{-6} mole/sec, respectively
N_2 flow rate 180 x 10^{-6} mole/sec
NO titration 15.7 x 10^{-6} mole/sec
Total pressure 2 torr
(All values reproducible within ±3 - 5%)

NH_3 input (mole/sec) x 10^6	HCN recovered (mole/sec) x 10^6	SO_2 input (mole/sec) x 10^6	HCN recovered (mole/sec) x 10^6
0.00	9.5	0.00	9.3
0.86	8.0	0.82	9.5
2.0	7.9	2.0	10.0
6.2	9.2	7.3	10.7
11.3	9.9	11.3	11.3
24.5	11.4	14.2	11.3
46	12.7	18.3	11.7
78	13.2	28.3	11.9
134	14.0	38	11.9
180	14.7	-	-

Figure 8

Reaction of Ethylene with Active Nitrogen
HCN yield as a function of NH_3 and SO_2 flow rates

○ - In the presence of NH_3
△ - In the presence of SO_2


fHCN(mole/sec)×10^6
14·0
12·0
10·0
8·0
6·0
0
20
40
60
80
100
120
140
160
180
flow rate (mole/sec)×10^6

No significant change in the endpoint was observed, nor was the reaction flame displaced from its original location, even for total flow rates of NO and nitrogen greater than the highest flow rates of ammonia and ethylene of the earlier experiments. From these various experiments, it may safely be assumed that back diffusion was negligible.

Several repetitions of the experiments with ethylene confirmed both the initial decrease, and the subsequent increase in the production of HCN in the presence of NH_3 . In the presence of sulphur dioxide, however, no initial decrease in the HCN yield was observed. Instead, the HCN production increased with SO_2 flow rate, to a somewhat lower maximum value than that observed in the presence of ammonia.

(c) The methane reaction

With CH_4 as reactant, maximum HCN production in the absence of NH_3 or SO_2 was attained at methane flow rates in excess of 50×10^{-6} mole/sec. The reaction was accompanied by the usual emission of the CN bands, which became visible when the flow rate of methane exceeded 10×10^{-6} mole/sec. In the presence of ammonia, however, this emission was markedly weakened and was completely quenched for NH_3 flow rates above 5×10^{-6} mole/sec. The same general behaviour was observed with SO_2, although higher flow rates of it were necessary to quench the CN emission completely. The results in Table XII and Fig. 9 show the pronounced inhibition of

HCN production in the presence of NH_3 and SO_2. It is interesting that, although the reaction was more sensitive to the presence of NH_3 than to SO_2, the maximum inhibition by the two gases appeared to approach approximately the same extent.

TABLE XII

Reaction of Methane with Active Nitrogen in the Presence of $NH_3$and SO

CH_4 flow rate 64 x 10^{-6} mole/sec
(Other conditions as in Table XI)

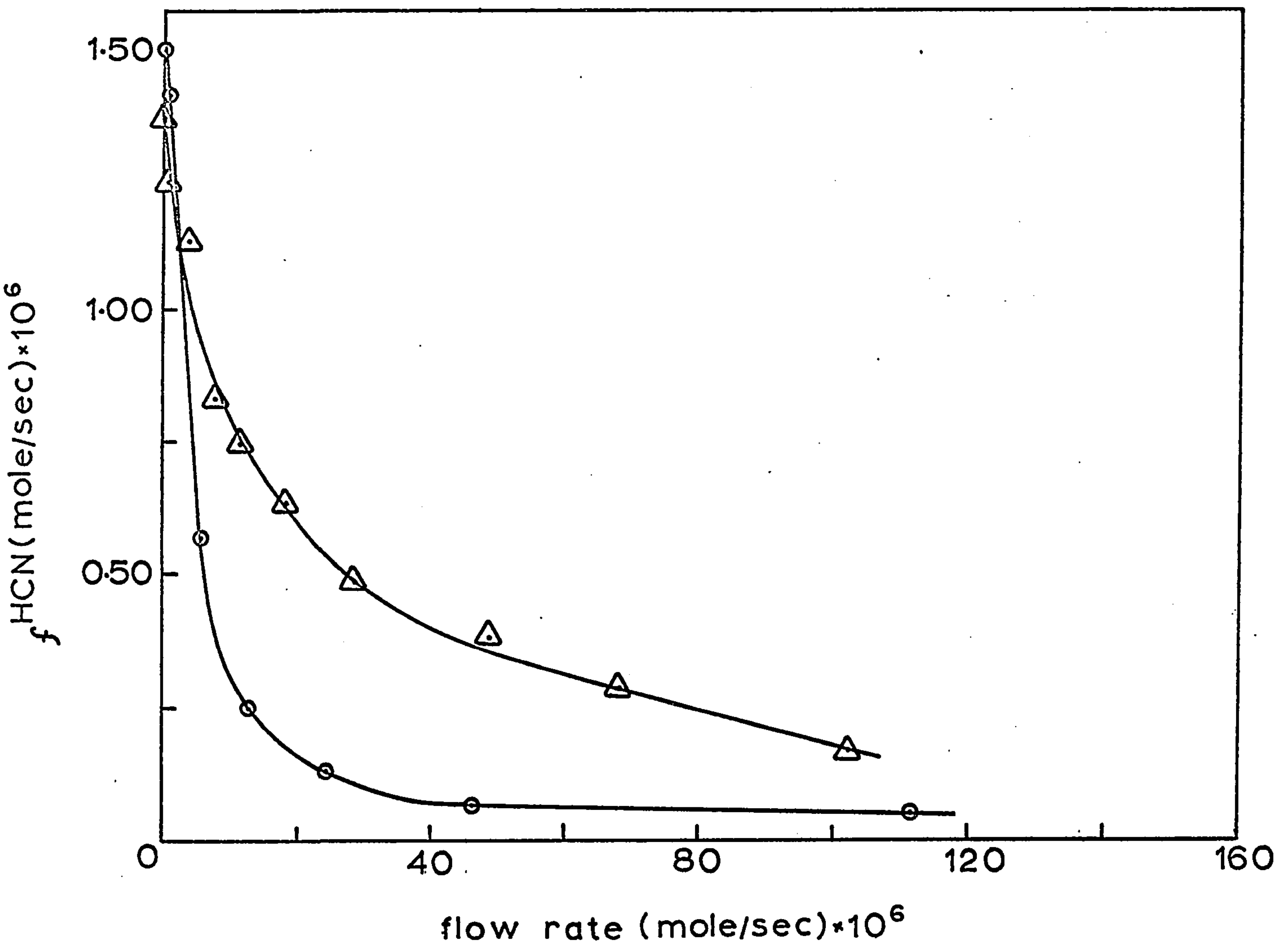
NH_3 input (mole/sec) x 10^6	HCN yield (mole/sec) x 10^6	SO_2 input (mole/sec) x 10^6	HCN yield (mole/sec) x 10
0.00	1.49	0.00	1.35
0.82	1.42	0.82	1.24
6.2	0.56	3.9	1.12
11.3	0.240	7.3	0.82
24.5	0.150	11.3	0.74
46	0.094	18.3	0.63
111	0.083	28.3	0.48
-	-	49	0.380
-	-	68	0.280
-	-	102	0.180

Figure 9

Reaction of Methane with Active Nitrogen
HCN yield as a function of NH_3 and SO_2 flow rates

○ - In the presence of NH_3

△ - In the presence of SO_2


1·50
1·00
0·50
0
40
80
120
160
f HCN (mole/sec)×10^6
flow rate (mole/sec)×10^6

(d) The cyclopropane reaction

The yield of hydrogen cyanide from this reaction did not reach a plateau value with hydrocarbon flow rate at room temperature. The reaction was accompanied by a violet CN emission, and the HCN production increased with cyclopropane flow rate. The emission seemed to remain practically unchanged when ammonia flow rates were below about 11×10^{-6} mole/sec, but was gradually displaced by the yellow nitrogen afterglow as NH_3 flow rates were further increased. A similar gradual change to the yellow afterglow occurred in the presence of SO_2 (in excess of 7×10^{-6} mole/sec). However, complete restoration of the yellow emission was not attained, with either NH_3 or SO_2, even at high flow rates. The extent to which HCN formation was inhibited in the presence of each gas is shown in Table XIII and Fig. 10.

(e) The ethane, propane and n-butane reactions

The effects of NH_3 and SO_2 on the active nitrogen reactions with these hydrocarbons were studied by varying the hydrocarbon flow rates at fixed levels of NH_3 or SO_2 input.

(i) The ethane reaction

In the absence of NH_3 or SO_2, the reaction with C_2H_6 was accompanied by the CN emission and by a gradual increase in the HCN production with ethane flow rate. No plateau HCN yield was obtained, even for ethane flow rates above 100×10^{-6} mole/sec. The CN emission seemed to intensify as the hydrocarbon flow rate

TABLE XIII

Reaction of Cyclopropane with Active Nitrogen in the Presence of NH_3 and SO_2

Cyclopropane flow rate 37 x 10^{-6} mole/sec
N_2 flow rate 185 x 10^{-6} mole/sec
NO titration 16.0 x 10^{-6} mole/sec
Total pressure 2 torr

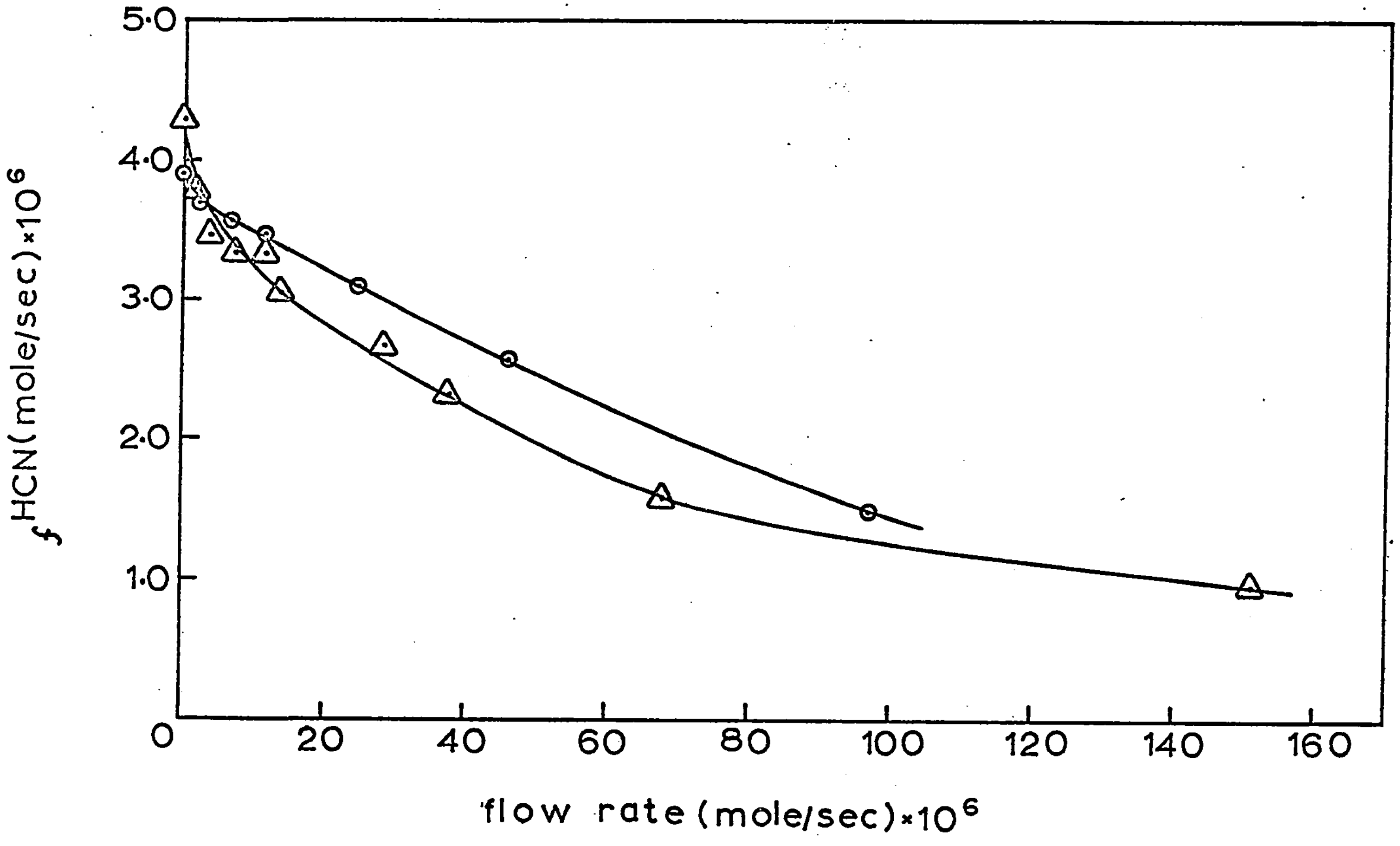
NH_3 input (mole/sec) x 10^6	HCN yield (mole/sec) x 10^6	SO_2 input (mole/sec) x 10^6	HCN yield (mole/sec) x 10^6
0.00	3.90	0.00	4.30
0.80	3.84	1.70	3.76
2.0	3.71	3.9	3.45
6.2	3.55	7.3	3.36
11.3	3.44	11.3	3.36
24.5	3.07	14.2	3.04
46	2.56	28.3	2.65
97	1.47	37.7	2.31
-	-	68	1.57
-	-	151	0.95

Figure 10

Reaction of Cyclopropane with Active Nitrogen
HCN yield as a function of NH_3 and SO_2 flow rates

○ - In the presence of NH_3

△ - In the presence of SO_2


5·0
4·0
3·0
2·0
1·0
0
20
40
60
80
100
120
140
160
f_{HCN}(mole/sec)×10^6
flow rate (mole/sec)×10^6

was increased, until a seemingly steady intensity was attained for ethane flow rates above about 35 x 10^{-6} mole/sec. Flow rates of NH_3 or SO_2 below those corresponding to maximum destruction of either gas under the same experimental conditions caused no significant change in the HCN production and the reaction flame was not markedly affected. With flow rates of NH_3 of 11 x 10^{-6} and 24 x 10^{-6} mole/sec, the production of HCN was inhibited, and the CN emission was completely quenched unless the ethane flow rate exceeded approximately 60 x 10^{-6} and 80 x 10^{-6} mole/sec, respectively. When the flow rate of NH_3 was increased to 46 x 10^{-6} mole/sec, inhibition of HCN production was further increased, and only an extremely weak flame remained, even for very large ethane flow rates. In the presence of SO_2, on the other hand, the CN chemiluminescence persisted with both flow rates used (2.5 x 10^{-6} and 11 x 10^{-6} mole/sec), although it was quite weak at ethane flow rates below 20 x 10^{-6} mole/sec.

In Table XIV and Fig. 11 values of ΔHCN represent the extent of inhibition (i.e., decrease in HCN yield) brought about by the addition of NH_3 or SO_2. It will be noted that the inhibition with a given flow of either NH_3 or SO_2 passed through a maximum with increasing C_2H_6 flow, and NH_3 or SO_2 flow rate. It is interesting, perhaps, that for the one flow rate (11 x 10^{-6} mole/sec) for which data were obtained for both NH_3 and SO_2, the inhibition by ammonia was more pronounced at lower C_2H_6 flows, and less marked at higher C_2H_6 flows, than that due to SO_2. This change in relative inhibiting efficiencies of NH_3 and SO_2 with ethane flow

TABLE XIV

Reaction of Ethane with Active Nitrogen in the Presence of NH_3 and SO_2

N_2 flow rate 185 - 200 x 10^{-6} mole/sec
Total pressure 2 torr
Note: (All quantities are (mole/sec) x 10^6)

	AMMONIA ADDED						SULPHUR DIOXIDE ADDED			
	NH_3 = 11		NH_3 = 24		NH_3 = 46		SO_2 = 2.5		SO_2 = 11	
C_2H_6 input	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN
2.5*	1.0	0.6	1.0	0.7	1.2	1.0	-	-	-	-
6.2	1.98	1.30	2.21	1.47	1.99	1.69	1.97	0.36	1.97	0.95
11.0	-	-	-	-	-	-	2.65	0.55	2.65	1.15
13.0	-	-	2.70	1.50	-	-	-	-	-	-
15.0	-	-	-	-	3.00	2.10	-	-	-	-
16.8	2.87	1.26	3.02	1.61	-	-	3.22	0.61	3.22	1.33
30.0	3.55	1.05	-	-	-	-	-	-	-	-
39	4.11	1.07	4.31	1.50	4.54	2.24	5.00	0.40	5.00	1.34
45	-	-	4.81	1.70	-	-	-	-	-	-
47	-	-	-	-	5.00	2.15	-	-	-	-
55	4.80	1.00	-	-	-	-	-	-	-	-
60	-	-	-	-	5.40	2.05	-	-	-	-
64	-	-	5.32	1.42	-	-	6.20	0.20	6.20	1.00
80	-	-	-	-	6.00	1.80	-	-	-	-
85	-	-	5.63	1.10	-	-	-	-	-	-
89	-	-	5.81	1.22	6.20	1.78	-	-	-	-

* Reproducibility within ±5%, corresponding reproducibility in HCN production within ±10%. Higher hydrocarbon flow rates are reproducible within ±3% and the corresponding reproducibility in HCN formation within ±2%.

Figure 11

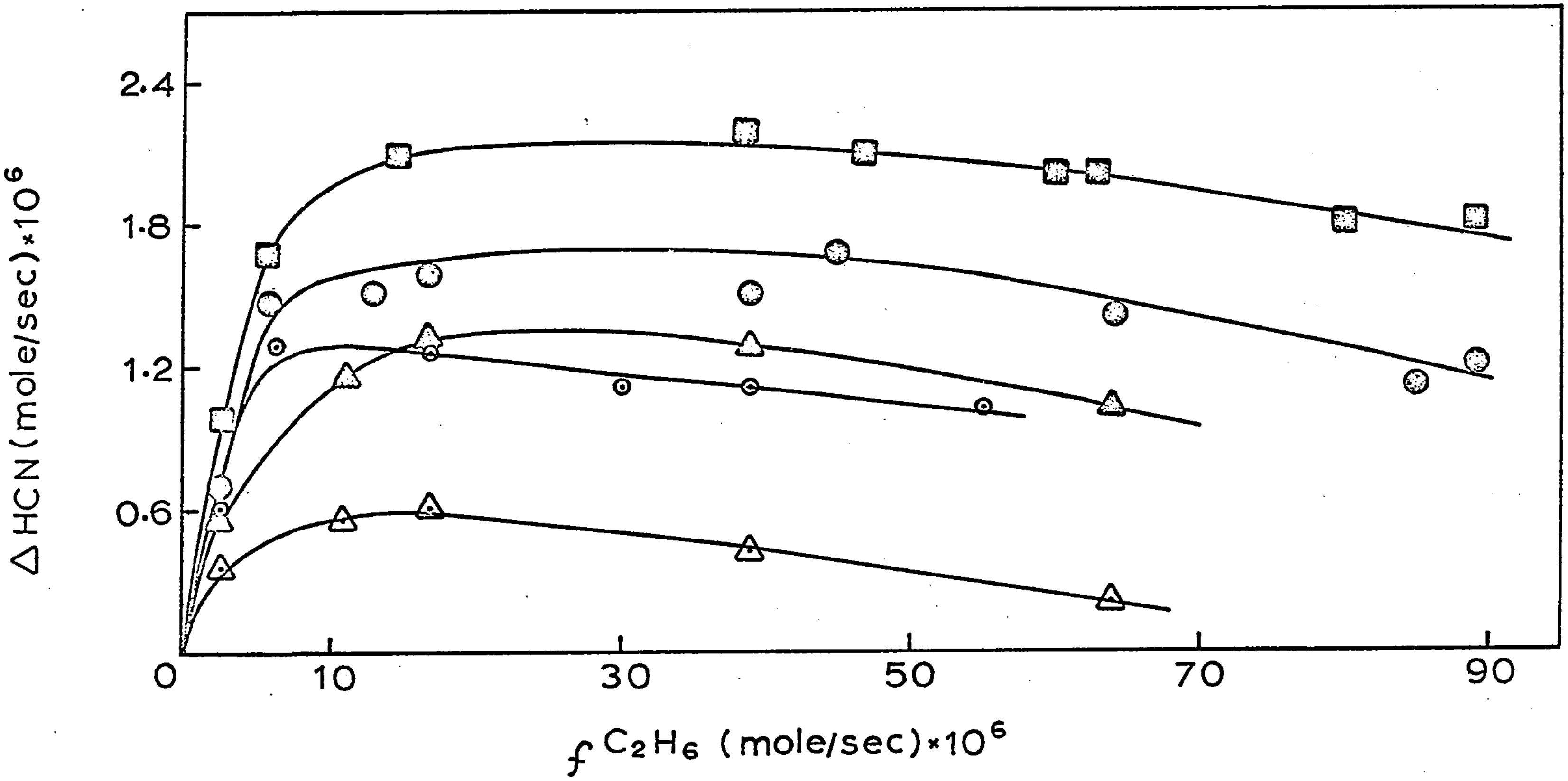
Reaction of Ethane with Active Nitrogen
HCN as a function of C_2H_6 flow rate

In the presence of NH_3:

○ - 11 x 10^{-6} mole/sec
● - 24 x 10^{-6} mole/sec
■ - 46 x 10^{-6} mole/sec

In the presence of SO_2:

△ - 2.5 x 10^{-6} mole/sec
▲ - 11 x 10^{-6} mole/sec


2.4
1.8
1.2
0.6
0
10
30
50
70
90
Δ HCN (mole/sec)×10^6
f C2H6 (mole/sec)×10^6

rate might reflect the effects of secondary reactions involving atomic hydrogen and atomic oxygen derived from the parent gases as they exercised their inhibiting effects. This behaviour was cast into sharper relief by studying the corresponding inhibitions of the propane and butane reactions.

(ii) The propane and butane reactions

A bright CN emission accompanied these reactions in the absence of NH_3 or SO_2, and the HCN yields attained plateau values at hydrocarbon flow rates greater than about 20×10^{-6} mole/sec for propane and 12×10^{-6} mole/sec for n-butane. With both of these reactants, the behaviour upon addition of NH_3 or SO_2 assumed an aspect that was only observed in the experiments with ethylene described previously. At relatively low hydrocarbon flow rates, a tendency for NH_3 or SO_2 to inhibit HCN production generally gave way, at higher hydrocarbon flow rates, to increased production of HCN (corresponding to negative values of ΔHCN). The CN emission persisted in all the experiments, with little if any intensification as hydrocarbon flow rates were increased. It does not seem necessary to present in detail the many data obtained for these systems, but typical behaviour with addition of NH_3 and SO_2 (2.5×10^{-6} mole/sec) to the propane reaction is illustrated in Fig. 12. With butane, the extents of inhibition were somewhat less, while the increase in HCN with NH_3, at high butane flow rates, was more pronounced. The data for the propane and butane reactions, in the presence of NH_3 and SO_2 are summarized in Tables XV, XVI

Figure 12

Reaction of Propane with Active Nitrogen

HCN yield as a function of propane flow rate

○ - In the absence of NH_3 or SO_2

△ - In the presence of NH_3 (2.5×10^{-6} mole/sec)

□ - In the presence of SO_2 (2.5×10^{-6} mole/sec)

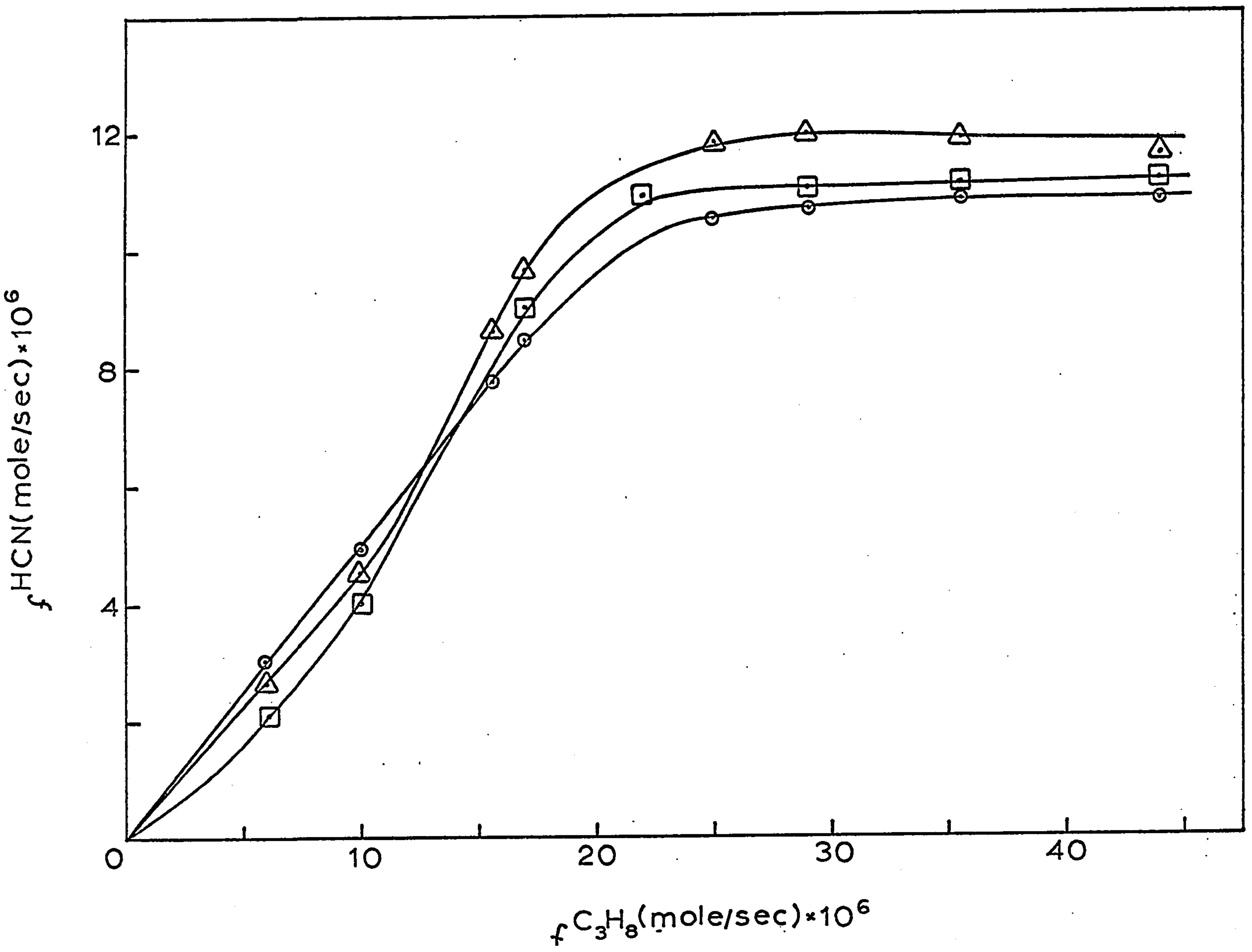

12
8
4
0
10
20
30
40
f_{HCN}(mole/sec)×10^6
$f_{C_3H_8}$(mole/sec)×10^6

TABLE XV

Reaction of Propane with Active Nitrogen in the Presence of NH_3 and SO_2

N_2 flow rate 190 x 10^{-6} mole/sec
Total pressure 2 torr
Note: (All quantities are (mole/sec) x 10^6)

	AMMONIA ADDED						SULPHUR DIOXIDE ADDED			
C_3H_8	NH_3 = 2.5		NH_3 = 11		NH_3 = 24		SO_2 = 2.5		SO_2 = 11	
input	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN
5.0	-	-	2.20	0.60	2.20	0.70	-	-	2.30	0.70
6.0	3.0	0.4	-	-	-	-	3.00	0.9	-	-
10.0	4.9	0.4	4.3	0.9	4.4	1.3	4.9	0.9	4.3	1.0
15.0	7.7	-0.9	-	-	-	-	-	-	-	-
17.0	8.4	-1.2	7.2	1.0	-	-	-	-	8.2	1.4
20.7	-	-	-	-	-	-	-	-	9.32	1.7
22.0	-	-	-	-	-	-	10.50	-0.40	-	-
25.0	10.50	-1.30	-	-	10.13	2.0	-	-	10.51	1.60
29.0	10.70	-1.20	10.02	-1.3	10.30	1.5	11.10	-0.30	10.72	1.70
35	10.80	-1.00	10.21	-2.8	10.40	-0.8	11.21	-0.30	10.80	0.50
40	-	-	10.43	-3.5	10.51	-1.8	-	-	-	-
44	10.80	-0.80	10.40	-4.0	10.73	-2.0	11.32	-0.30	-	-

Reproducibility of HCN yield within ±1 - 3%.

Figure 13

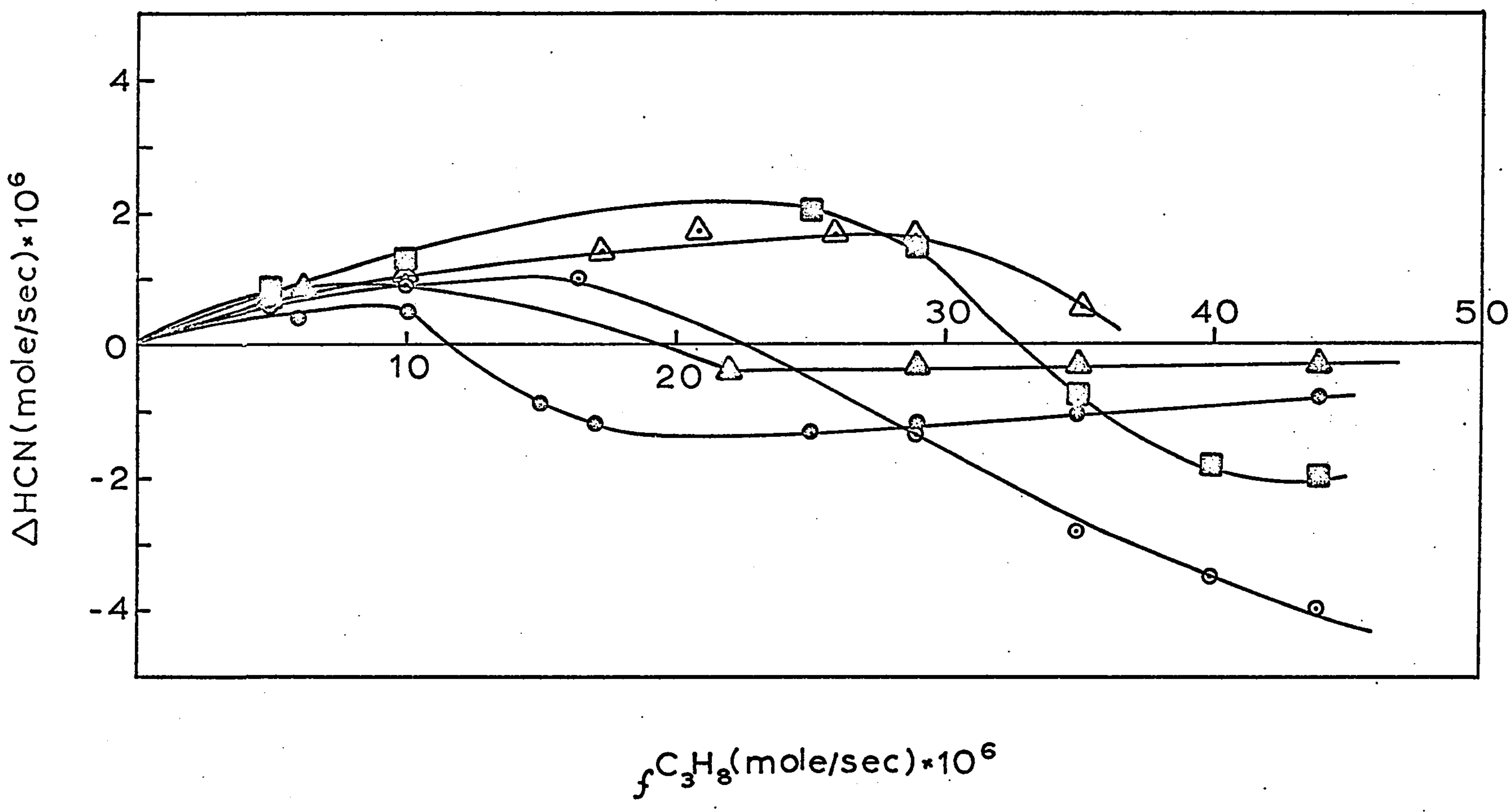
Reaction of Propane with Active Nitrogen
HCN as a function of C_3H_8 flow rate

In the presence of NH_3:

● - 2.5 x 10^{-6} mole/sec
○ - 11 x 10^{-6} mole/sec
■ - 24 x 10^{-6} mole/sec

In the presence of SO_2:

△ - 2.5 x 10^{-6} mole/sec
▲ - 11 x 10^{-6} mole/sec



4
2
0
-2
-4
ΔHCN(mole/sec)×10^6
10
20
30
40
50
fC3H8(mole/sec)×10^6

TABLE XVI

Reaction of n-Butane with Active Nitrogen in the Presence of NH_3 and SO_2

N_2 flow rate 190 x 10^{-6} mole/sec
Total pressure 2 torr
Note: (All quantities are (mole/sec) x 10^6)

	AMMONIA ADDED				SULPHUR DIOXIDE ADDED			
	NH_3 = 2.5		NH_3 = 11		SO_2 = 2.5		SO_2 = 11	
C_4H_{10} input	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN	HCN	ΔHCN
0.52*	0.85	-0.7	0.52	-0.6	0.78	-0.4	-	-
3.5*	3.9	-0.6	3.7	0.8	4.6	0.6	4.4	1.1
7.1	6.62	-0.30	7.90	1.8	7.70	1.0	8.00	2.71
13.1	8.71	-1.40	8.82	-3.20	9.32	-0.30	9.17	0.60
15.0	-	-	-	-	-	-	9.10	0.00
23.2	8.60	-1.10	8.85	-3.10	9.12	-0.50	9.07	-0.20
26.6	-	-	-	-	9.00	-0.40	-	-
28.7	8.63	-0.90	-	-	-	-	-	-
35	8.60	-0.50	8.76	-3.30	9.07	0.00	8.81	-0.70

* See Table XIV.

Figure 14

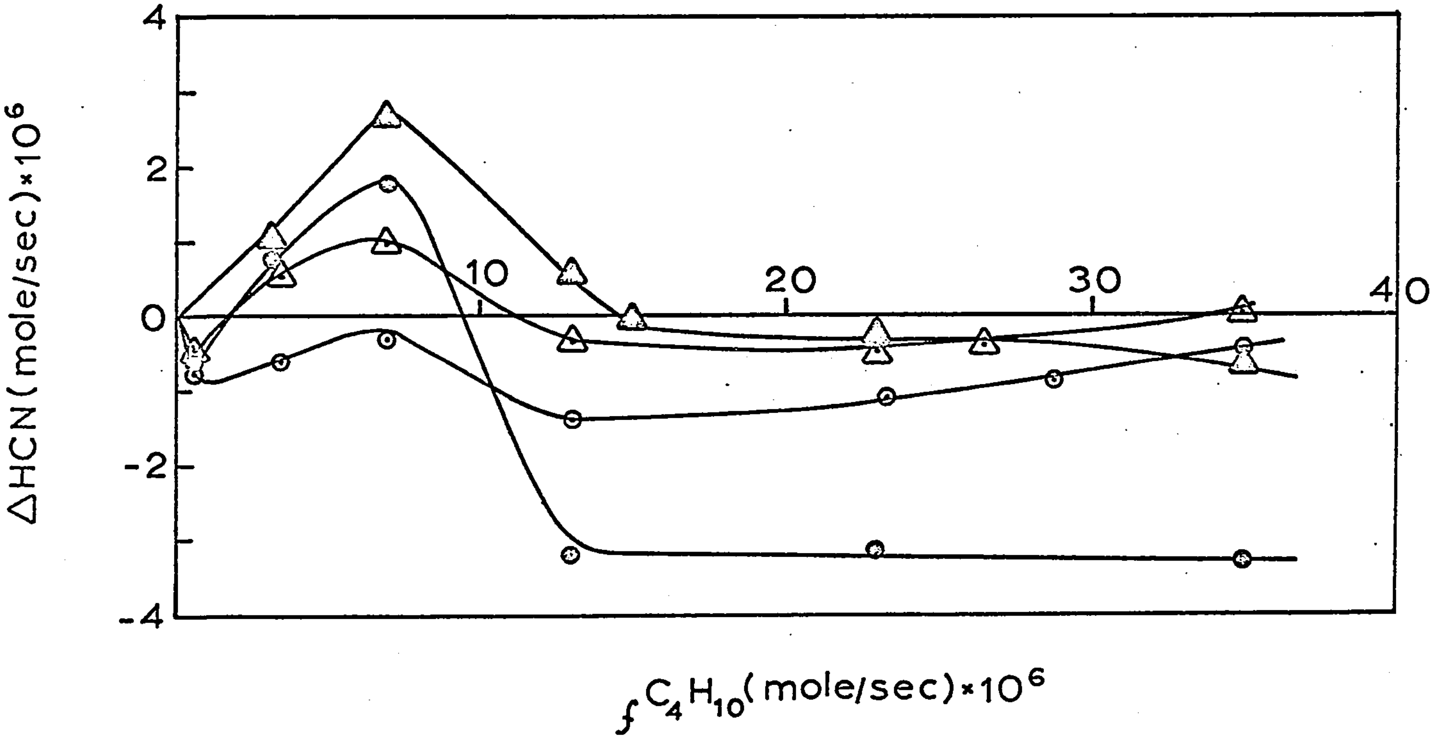
Reaction of n-Butane with Active Nitrogen
HCN as a function of n-C_4H_{10} flow rate

In the presence of NH_3:

○ - 2.5×10^{-6} mole/sec
● - 11×10^{-6} mole/sec

In the presence of SO_2:

△ - 2.5×10^{-6} mole/sec
▲ - 11×10^{-6} mole/sec


4
2
0
-2
-4
ΔHCN (mole/sec)×10^6
10
20
30
40
$f_{C_4H_{10}}$ (mole/sec)×10^6

and shown graphically in Figs. 13 and 14.

An overall scrutiny of the data indicates a general similarity between the reactions of ammonia and sulphur dioxide with active nitrogen and in their influence on other reactions conducted in their presence. Some not unexpected differences are observed, but these might well be due to the essential differences between the two molecules. Unfortunately, reactions of active nitrogen with various intermediates, (NH, NH_2, etc.) that might result from the NH_3-active nitrogen reaction cannot be conveniently studied, owing to their transient existence. On the other hand, the reaction of SO_2 with active nitrogen was probably accompanied by more stable by-products and intermediates that do lend themselves to further investigation in possible reactions with active nitrogen.

(3) THE SO_2 REACTION

(a) Maximum extent of the reaction

Although practically no decomposition of SO_2 occurred when it was admitted to active nitrogen derived from either a microwave discharge or from an "unpoisoned" condensed discharge, a relatively small decomposition of SO_2 occurred in a "poisoned" condensed electrode discharge. It was desirable to verify the earlier observations before proceeding with more detailed study of the SO_2-active nitrogen system. This was possible owing to much closer control and estimation of SO_2 flow rates that experience with the system now made possible. In one series of experiments, with an "unpoisoned" condensed discharge, the SO_2 inlet was brought closer to the exit of the discharge tube, but neither the presumably higher active nitrogen concentration at this point, nor the increase in the reaction time afforded by the earlier introduction of SO_2, resulted in detectable decomposition of SO_2, even for prolonged periods of operation. In other experiments, also made at this later date, the decay of active nitrogen from a microwave discharge was again followed by nitric oxide titration in the pressure range 2 to 3 torr, at various flow rates of SO_2. As before, virtually no change in the rate of decay was observed in the presence of SO_2.

Since there was some possibility that hydrogen atoms derived from the "poisoning" agent (H_2 or H_2O) might have been responsible for at least part of the observed decomposition of SO_2 in "poisoned" systems, experiments were made in which molecular nitrogen was substituted by argon in a condensed discharge. There was then no detectable decomposition of SO_2 when it was added downstream, nor was there formation of any solid reaction product, whether argon alone, or argon "poisoned" with a trace of hydrogen, was passed through the discharge.

The addition of sulphur dioxide to an active nitrogen stream from a discontinuous condensed discharge "poisoned" with hydrogen did not quench the afterglow. It merely slightly reduced the intensity of the yellow colour, in a manner similar to that during an NH_3 reaction with active nitrogen, or during an NO titration, when the flow rate of nitric oxide was gradually increased. By throttling the pump, it was found that active nitrogen flow rates could be reduced (NO titration), but with a qualitative difference in the yellow afterglow when SO_2 was added upstream. In this manner, the active nitrogen was reduced from 19 to 14.5 to 6.8 x 10^{-6} mole/sec, at constant total pressure of 2 torr, with a concomitant decrease of about 30% in the linear velocity of the gas. However, the maximum destruction of SO_2 remained practically constant (within ±10%) at 1.2 x 10^{-6} mole/sec over the entire range of active nitrogen flow rates. Moreover, when SO_2 was introduced into the reaction vessel at two points 20 cm apart, and the reaction with active nitrogen was then allowed to proceed with the same reaction time, smaller decomposition was observed when SO_2 was introduced at the lower point.

The practically continuous ("pseudo-continuous") discharge through molecular nitrogen in a "poisoned" or "unpoisoned" system produced a flow of active nitrogen that was virtually free of pulsations, and one that could be readily and reproducibly estimated by the NO titration. The observed maximum destruction of SO_2 in this system did not exceed 1.0 x 10^{-6} mole/sec, when sulphur dioxide flow rates were comparable with the available N atom flow rates. For conditions of complete reaction, with high flash rate, the maximum extent of decomposition of SO_2 was related to SO_2 flow rate in the manner shown in Fig. 15. This was similar to that observed previously in a discontinuous discharge "poisoned" with either water vapour or a trace of hydrogen.

TABLE XVII

Reaction of Sulphur Dioxide with Active Nitrogen

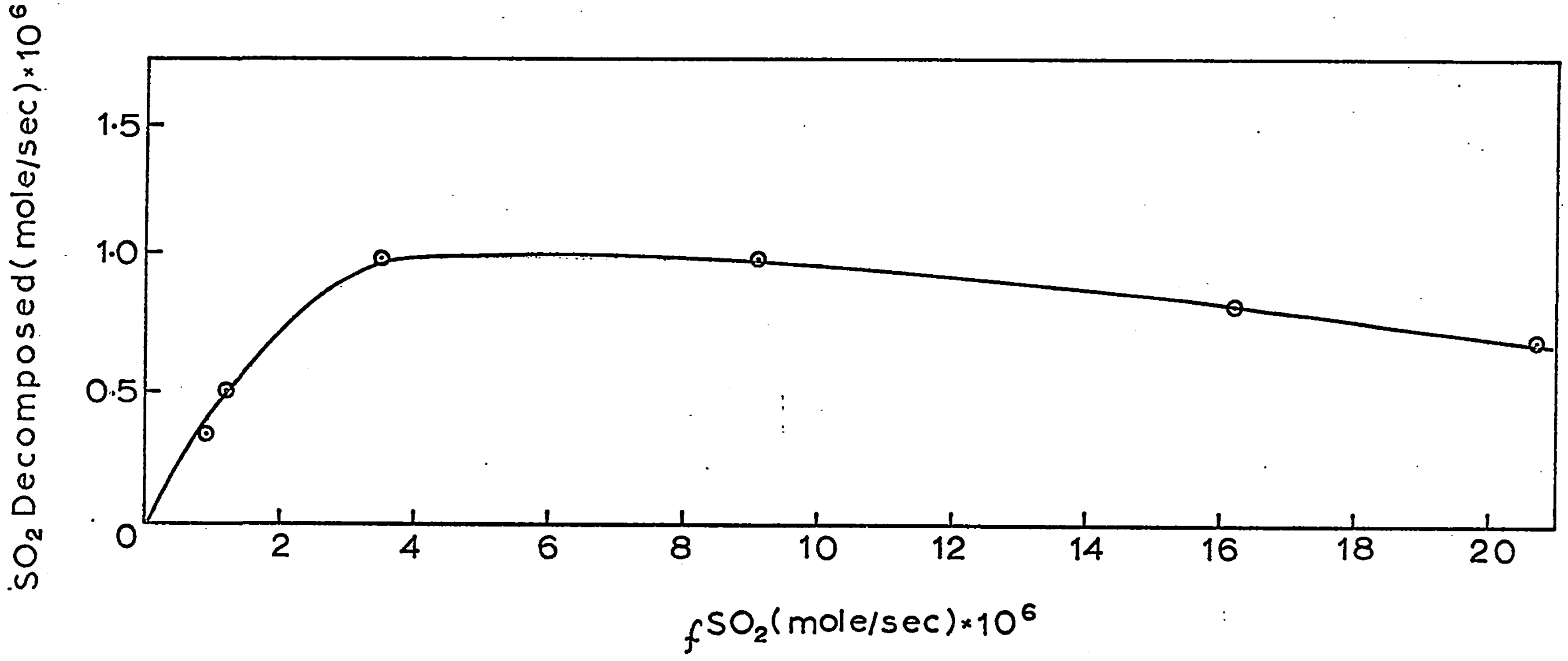
(Complete reaction with high flash rate discharge)
System "poisoned" with H_2 (less than 0.1 x 10^{-6} mole/sec)
N_2 flow rate 190 x 10^{-6} mole/sec
NO titration 22 x 10^{-6} mole/sec
Total pressure 2 torr
Reaction temperature 333^{o}K

SO_2 input (mole/sec) x 10^6	SO_2 reacted (mole/sec) x 10^6
0.880	0.340
1.200	0.500
3.50	1.00
9.10	1.00
16.20	0.83
20.70	0.70

Figure 15

Reaction of Sulphur Dioxide with Active Nitrogen
(Complete reaction)

SO_2 decomposed as a function of SO_2 flow rate



SO₂ Decomposed (mole/sec) × 10⁶
1·5
1·0
0·5
0
2
4
6
8
10
12
14
16
18
20
fSO₂ (mole/sec) × 10⁶

(b) Products of the reaction

Apart from SO, which would almost certainly be formed as a product of the SO_2 - active nitrogen reaction (see later), a plausible product of the reaction, for which qualitative evidence was soon obtained, was sulphur trioxide. Extensive darkening of the stopcock grease in the ground joints of the product traps T_5, T_6, and in the associated stopcocks suggested its attack by SO_3 (probably by sulphonation). This discolouration which became serious only after a relatively large number of experiments with SO_2 in the presence of active nitrogen, suggested the presence of O atoms during the decomposition of SO_2 by active nitrogen, and prompted a more definitive analysis for the possible presence of SO_3 in the products*.

As indicated previously, a solid product was collected in the liquid nitrogen trap during reaction of SO_2 with active nitrogen. Upon exposure to air, the yellow-white colour of this solid faded, and an acidic oily film remained. When an aqueous solution of this residue was treated with $BaCl_2$ or $Hg(NO_3)_2$, the characteristic reactions of $SO_4^=$ were obtained. The presence of $SO_4^=$ was confirmed by the specific Sodium-Rhodizonate spot test. The presence of SO_3 in the products was also indicated by the spectra reported in Fig. 16. These indicate a substantial concentration of sulphuric acid, and this was presumably formed on the NaBr pellet when it was exposed to moisture in the atmosphere.

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* Blank experiments showed that SO_3, but not SO_2 was able to cause a similar darkening of the grease used.

Figure 16

Infrared Spectra of:

a. Product deposited on NaBr pellet (from the reaction of SO_2 with active nitrogen).

b. 75% H_2SO_4.

c. 80% H_2SO_4.

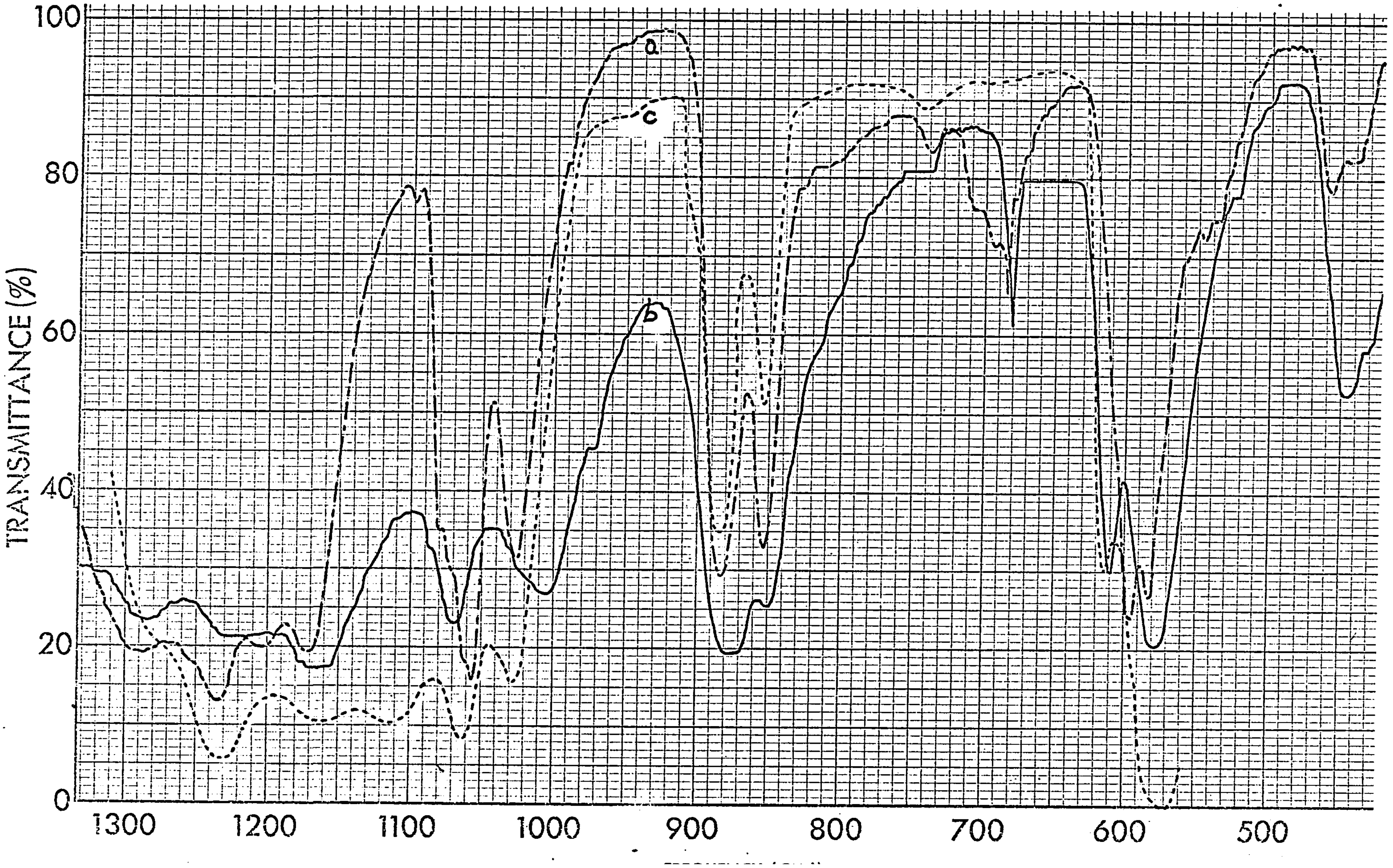

TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
a
c
b

Figure 17

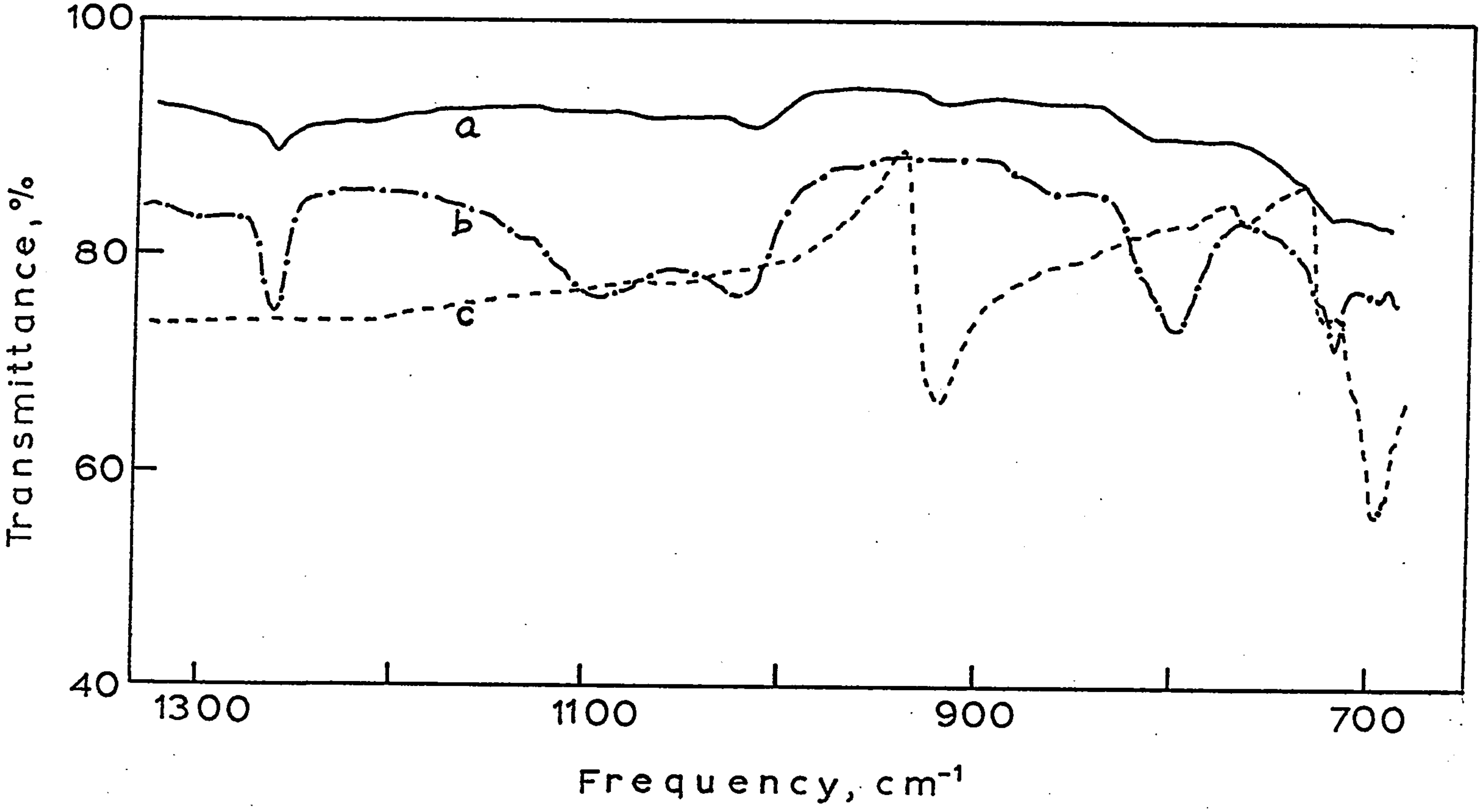
Reaction of Sulphur Dioxide with Active Nitrogen
Infrared Spectra of Reaction Products
Deposited in the Reaction Tube

Solvent: Benzene

a. Spectrum of products collected during the experiments in a virtually continuous condensed discharge "poisoned" with a trace of hydrogen.

b. Spectrum of products collected during the experiments in a virtually continuous "unpoisoned" condensed discharge system.

c. Spectrum of a pure sample of S_4N_4.


100
80
60
40
Transmittance, %
1300
1100
900
700
Frequency, cm⁻¹
a
b
c

The absorption peaks for the reaction product compared reasonably well with those for a known sample of sulphuric acid in a narrow concentration range about 80% H_2SO_4.

It seems quite unlikely that the $SO_4^=$ ion could be formed directly in the SO_2 - active nitrogen reaction. The only reasonable explanation for its presence is to assume that the reaction products contained SO_3 formed by the reaction of SO_2 with oxygen atoms produced in the SO_2 - active nitrogen reaction*.

The decomposition of SO_2 by active nitrogen was accompanied also by the formation of another transparent yellow solid which seemed to be non-crystalline and water soluble. This product very uniformly coated the upper third of the reaction tube. Its I.R. spectrum showed a characteristic peak at 920 cm^{-1} (Fig. 17a) which identified the presence of tetra-sulphur tetra-nitride, S_4N_4. Spectrum b, in the same figure, corresponds to products obtained in a "poisoned" system in which the ratio N:S (S assumed to be formed by secondary attack of SO by N) was about 21:1. Comparison of this spectrum with the relatively few spectra of S - N compounds yet available in the literature, reveals also the presence of $(SN)_x$ with its peak at 1015 cm^{-1} (149), and of S_2N_2 with a peak at 795 cm^{-1} (150). Sufficient alteration of the N:S ratio might well result in still other S - N compounds.

An attempt was made to increase the N:S ratio, with the active nitrogen formed in the so-called "pseudo-continuous

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*It might be noted that in a system "poisoned" with traces of H_2, formation of SO_3 could not occur by reactions such as $O + H_2 \rightarrow OH + H$; $OH + SO_2 \rightarrow SO_3 + H$, since the latter is endothermic to an extent of about 20 kcal/mole.

unpoisoned" condensed discharge. A decrease in the N atom concentration to 15 x 10^{-6} mole/sec in this system was accompanied by a decrease of sulphur formation to about 0.25 x 10^{-6} mole/sec (inferred from the decomposition of SO_2). This resulted in an N:S ratio of 60:1, and there resulted a different I.R. spectrum for the solid product. Again, several sulphur nitrides were probably formed in this system, as indicated by the spectrum in Fig. 17a. The peak at about 920 cm^{-1} may be attributed to S_4N_4, while that at 1015 cm^{-1} confirmed the presence of at least one other sulphur nitride. In general, the results are in accord with those of a previous study (133) on the sulphur-active nitrogen system*.

No attempt was made to obtain kinetic data on the formation of the nitrides in the present system. However, it was noted that the extent of their deposition on an NaBr pellet was relatively slow, and a function of the duration of the experiment. For this reason it seemed unnecessary to take their production into account in formulating the kinetics of the reactions of SO and SO_2 with active nitrogen.

(c) Kinetic measurements on the reaction

Kinetic measurements on the SO_2 reaction were made by stopping the reaction with a cobalt target. The presence of SO_2 did not seem to affect the efficiency of the target, nor did the

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*Another infrared analysis of an extract of total products in CS_2 did not give any indication of the presence of elemental sulphur.

yellow afterglow extend past its surface, even for very short reaction distances at relatively high active nitrogen flow rates. To ensure that the target did stop the reaction efficiently, it was tested at different levels in the reaction vessel by introducing C_2H_4, NH_3 and SO_2 separately to the system at a point below the target. Subsequent analyses showed that no significant production of HCN from C_2H_4, nor destruction of NH_3 or SO_2 occurred, and that the target might, therefore, be assumed to remove active nitrogen completely from the gas stream.

During relatively short reaction times with SO_2, the formation of the yellowish transparent product on the wall of the vessel became more distinct, presumably because it was confined to a smaller surface area. With decrease of the reaction distance to less than about 20 cm, the results became unsatisfactory, owing to irreproducibility, although the precision was still within about 15%. The reproducibility was markedly improved after the reaction tube had been cleaned and dried. The experiments were then accompanied by an increase of target temperature, to about 150°C. This local heating effect was later checked for shorter warm-up periods, during which the temperature of the target was about the same as that of the ambient temperature. The results obtained indicated negligible effect of the larger temperature increase in the earlier experiments. Removal of the target, with subsequent external heating at the same level, gave results that were effectively the same as those obtained at room temperature in the absence of the target.

The results reported in Tables XVIII, XIX were obtained at a pressure of 2 torr for different initial SO_2 flow rates with different reaction times at 300°K and at elevated temperatures, respectively.

TABLE XVIII

Reaction of Sulphur Dioxide with Active Nitrogen

System "poisoned" with hydrogen
NO titration 20×10^{-6} mole/sec
Linear velocity 200 cm/sec
Total pressure 2 torr
Temperature 333°K

Reaction time (msec)	SO_2 input (mole/sec) $\times 10^6$	SO_2 residual (mole/sec) $\times 10^6$
313	4.53	3.91
291	4.74	4.16
306	5.01	4.38
330	5.19	4.51
274	6.08	5.48
265	6.84	6.26
270	7.35	6.75
199	8.45	7.97
259	9.39	8.76
147	10.03	9.63
208	10.25	9.73
200	13.02	12.50
168	17.29	16.84
144	20.0	19.6
157	22.3	21.9

TABLE XIX

Reaction of Sulphur Dioxide with Active Nitrogen at Elevated Temperatures

(Other conditions as in Table XVIII)

	Reaction time (msec)	SO_2 input (mole/sec) x 10^6	SO_2 recovered (mole/sec) x 10^6
473°K:	30	4.52	4.19
	121	4.55	3.93
	288	4.61	3.82
	52	4.63	4.21
543°K:	121	4.52	3.87
	52	4.55	4.07
	320	4.61	3.78
	35	4.63	4.27
688°K:	24	4.53	4.13
	187	4.53	3.69
	233	4.57	3.71
	40	4.62	4.08
	90	4.65	3.94

III. REACTION OF SULPHUR MONOXIDE WITH ATOMIC NITROGEN

Since SO_2 appeared to be incapable of reaction with atomic nitrogen (microwave discharge), and to undergo decomposition only under conditions when relatively high concentrations of electronically excited nitrogen molecules might be present (condensed electrode discharge) it immediately became of interest to determine whether the same might be true for the other oxides of sulphur, namely, the monoxide and the trioxide. Examination of this problem was begun with the monoxide, SO.

As indicated earlier ("Experimental"), SO was prepared in an auxilliary apparatus, in which oxygen atoms were generated by the reaction of N atoms (from a microwave discharge) with NO, and introduced into a stream of COS at about 225°C. Under these conditions, a sharp cut-off of a blue emission was observed when COS was introduced equivalent to the O atom flow rate. The products of the reaction, SO and CO, were then caused to react in the main reaction vessel with N atoms from a microwave discharge. Since CO is known to undergo no significant decomposition by active nitrogen (51), any reaction of N atoms that did occur could be attributed to the presence of SO.

The O atom, or COS flow rate could be adjusted to quench the afterglow completely in the main reactor, and the flow rate necessary to do so was one-half the flow rate of N atoms in that vessel. The conditions of equivalence between SO and N atom flow rates could not be achieved with either CO or COS.

In experiments in which the SO did not completely quench the afterglow, emission was observed of an ill-defined colour (mauve ?), possibly resulting from a blue emission ($NO^* \rightarrow NO + h\nu$) superimposed on the yellow afterglow. When the SO was replaced by an equivalent flow of CO or COS, no trace of a flame was observed, and the yellow afterglow was not noticeably quenched. With excess COS, a light blue emission was observed, which did not intensify with further increase of COS flow rate.

By titrating the residual N atoms with NO after different reaction times, the reaction of SO with N atoms was shown to be fast. Indeed, because the reaction went to completion with very short reaction times, it became expedient to increase the linear velocity of the gas stream to improve the accuracy of the measurements. This also helped to provide better mixing of the reactants during the course of the reaction.

The results, from which rate data might be derived, are summarized in Table XX. Additional data obtained from the study are contained in the Appendix.

TABLE XX

Reaction of Sulphur Monoxide with Atomic Nitrogen

Reaction temperature 300°K

SO input* (mole/sec) x 10^6	N atom input (mole/sec) x 10^6	N atom residual (mole/sec) x 10^6
SO generator at 225°C N_2 flow rate 304 x 10^{-6} mole/sec Total pressure 2 torr Reaction time 11.5 msec		
0.33	1.21	0.70
0.37	1.42	0.82
0.45	1.35	0.65
0.46	1.25	0.56
0.46	1.02	0.37
0.50	1.05	0.34
SO generator at 400°C N_2 flow rate 365 x 10^{-6} mole/sec Total pressure 2.5 torr Reaction time 7.2 msec		
0.071	1.52	1.42
0.081	1.53	1.40
0.120	1.41	1.24
0.172	1.35	1.12
0.25	1.23	0.95
0.30	1.03	0.67
SO flow line to reactor altered N_2 flow rate 420 x 10^{-6} mole/sec Total pressure 3.5 torr Reaction time 7.4 msec		
0.24	1.38	1.06
0.32	1.20	0.80
0.43	1.22	0.70
0.44	1.17	0.64
0.44	1.10	0.57
0.45	1.02	0.52

* Reproducibility within ±4%.

IV. REACTION OF SULPHUR TRIOXIDE WITH ATOMIC NITROGEN

Since sulphur trioxide was found to be a product of the reaction of SO_2 with active nitrogen, it was obviously of interest to study the SO_3 - active nitrogen reaction, and if possible to evaluate a rate constant for it. Again, as with the SO reaction, it was of particular interest to determine whether the trioxide might react with N atoms, or whether, like the dioxide, it required some other species to effect its decomposition. Accordingly, the study was commenced (and completed) with active nitrogen from a microwave discharge.

Considerable difficulties were encountered during the study owing to the high reactivity of SO_3 and its marked tendency for sulphonation reactions. It soon became apparent that special techniques had to be used and certain conditions imposed to ensure proper control and analysis of the experiments.

The presence of SO_3 in the system required a fluorinated stopcock grease that was relatively inert to attack. "Kel-F" was found to be satisfactory. Also, oil and mercury manometers could not be employed for measurements of SO_3 flow rates, and initial flow rates were determined in blank experiments, by acid-base titrations in a demountable absorber in which the SO_3 was dissolved in outgassed H_2O.

The reaction of sulphur trioxide with active nitrogen was accompanied by a mauve reaction flame about 2 cm below the SO_3 inlet. The intensity of the flame increased as the nitrogen atom and SO_3 flow rates were increased. Attempts to terminate the reaction by a metal target were unsuccessful; neither cobalt nor platinum seemed to be effective. Reaction of SO_3 with cobalt probably occurred, and the underlying platinum was not efficient, even when the SO_3 flow was stopped.

The kinetic data reported in Table XXI were obtained by terminating the reaction with an NO titration. This quenched the reaction very effectively, but the endpoint had to be scrupulously maintained, since excess of nitric oxide reacted with SO_3 to form a red coloured product. A similar coloured product could be condensed in the liquid nitrogen trap during blank experiments with NO in the presence of SO_3. The red colour faded when the trap was warmed, and a yellow-brown cloud was formed. The formation of NO_2 in the trap seemed obvious, and re-freezing the contents of the trap did not restore the formation of the coloured product.

Additional data were obtained when the reaction was terminated by the liquid nitrogen trapping procedure outlined earlier ("Experimental"). The low temperature method offered to give highly reproducible results, as inferred from a virtually constant SO_2 production for a particular reaction time. This method enabled the extent of the reaction to be followed by estimating the formation of SO_2 as a function of time (i.e., distance between the inlet jet for SO_3 and the liquid nitrogen surface), as shown in Table XXII.

At higher temperatures, as at lower temperatures, the reaction was accompanied by a mauve emission, which became apparent at relatively lower flow rates of nitrogen atoms and SO_3 as the temperature was increased. Representative data for the temperature range of 413 to 523^{o}K, with somewhat higher total pressure than at 300^{o}K, are shown in Table XXIII.

TABLE XXI

Reaction of Sulphur Trioxide with Atomic Nitrogen

(Reaction terminated by nitric oxide)
Total pressure 2 torr
Temperature 300°K

Reaction time (msec)	NO flow* (mole/sec) x 10^6	NO recovered (mole/sec) x 10^6
a. N_2 flow rate 182 x 10^{-6} mole/sec		
SO_3 flow rate 11.50x 10^{-6} mole/sec		
250	1.36	0.76
212	1.36	0.80
173	1.35	0.83
115	1.37	0.94
b. N_2 flow rate 188 x 10^{-6} mole/sec		
SO_3 flow rate 7.45 x 10^{-6} mole/sec		
240	1.26	0.70
204	1.40	0.85
167	1.56	1.07
110	1.70	1.30

* Reproducibility of NO flow rates within ±2%.

TABLE XXII

Reaction of Sulphur Trioxide with Atomic Nitrogen

(Reaction terminated by low temperature trapping)
Temperature 300°K

Reaction time (msec)	SO_3 input* (mole/sec) x 10^6	N atom input (mole/sec) x 10^6	SO_2 formed (mole/sec) x 10^6
	N_2 flow rate 150×10^{-6} mole/sec		
	Total pressure 2 torr		
350	5.20	3.30	0.90
430	5.20	3.00	0.88
286	7.00	3.30	0.92
430	7.00	3.20	1.10
	N_2 flow rate 225×10^{-6} mole/sec		
	Total pressure 2.5 torr		
118	9.90	4.9	0.85
118	9.90	4.9	0.85
430	13.30	4.20	2.15
430	13.30	4.20	2.15
	N_2 flow rate 260×10^{-6} mole/sec		
	Total pressure 2.7 torr		
333	12.80	3.80	1.57
222	17.00	4.20	1.63

* Reproducibility within less than ±1%.

TABLE XXIII

Reaction of Sulphur Trioxide with Atomic Nitrogen at Elevated Temperatures

(Reaction terminated by low temperature trapping)
N_2 flow rate 254 - 265 x 10^{-6} mole/sec
Total pressure 2.7 torr

	Reaction time (msec)	SO_3 input (mole/sec) x 10^6	N atom input (mole/sec) x 10^6	SO_2 formed (mole/sec) x 1
413°K:	333	8.00	3.90	2.54
	320	12.50	4.00	2.35
	107	15.50	4.60	1.83
	107	15.50	4.60	1.81
523°K:	111	6.56	4.50	1.70
	111	6.56	4.9	1.90
	222	6.56	4.40	2.35
	222	6.56	4.60	2.80
	320	12.50	4.00	2.90
	107	15.50	4.60	2.66

V. REACTION OF SULPHUR TRIOXIDE WITH ATOMIC OXYGEN

This reaction, like its counterpart reaction with nitrogen atoms, was undertaken not only for its intrinsic interest, but because of its possible significance in the reaction of SO_2 with active nitrogen, of which oxygen atoms are conceivably a product.

Oxygen atoms were first produced by a microwave discharge through a He - 3% O_2 mixture. However, the resulting oxygen atom flow rates were impractically low (0.1 to 0.2 x 10^{-6} mole/sec) for study of the present system. On the other hand, when pure oxygen, at a flow rate of 200 x 10^{-6} mole/sec, was admitted to the discharge, the increase in the O atom flow rate was accompanied by the formation of ozone. Its presence was undesirable, not only because of the hazard its presence presented, but because of its possible interference with the products of the reaction. Finally, oxygen atom production at a satisfactory level was achieved by an NO titration of N atoms from a microwave discharge, during which the endpoint was strictly maintained. Nitric oxide and SO_3 were introduced to the reaction vessel through jets J_1 and J_2, respectively.

The reaction of O atoms with SO_3 was accompanied by formation of a white solid which sublimed at about 0 - 20°C. Subsequent analysis of the sublimate indicated the presence of SO_2 and molecular oxygen*. However, when this solid was kept at about -10°C, and analysis was then made on the reaction products,

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*Qualitative identification of O_2 was made by pyrogallol in a gas burette.

little change was noted in the SO_2 production. The amount of solid increased with the flow of the reactants but was not significantly affected by increase of reaction temperature.

An attempt was made to use nitrogen dioxide to terminate this reaction, by providing rapid removal of oxygen atoms, but the simultaneous formation of nitric oxide in the presence of SO_3 prevented its continued use. Ethylene was found to be almost as effective (151) as nitrogen dioxide in reacting with oxygen atoms, but other reactions in the presence of SO_3 rendered it impractical. Neither was it possible to remove O atoms on a silver or silver oxide target and thereby quench the reaction, owing to attack of the target by SO_3. Finally, recourse was had again to the low temperature trapping method, and this again proved to be a successful method for stopping the reaction. The kinetic data are summarized in Table XXIV, for different initial reactant flow rates in the temperature range 300 to 500°K.

TABLE XXIV

Reaction of Sulphur Trioxide with Oxygen Atoms

(Reaction terminated by low temperature trapping)
N_2 flow rate 175 x 10^{-6} mole/sec
Total pressure 2 torr
Reaction time 360 msec

	SO_3 input (mole/sec) x 10^6	O atom input* (mole/sec) x 10^6	SO_2 formation (mole/sec) x 10^6
300°K:	4.65	4.9	0.114
	6.00	4.7	0.210
	8.20	3.20	0.100
	9.80	3.10	0.185
	12.50	5.0	0.400
	14.40	2.80	0.270
	19.0	3.20	0.370
	20.6	5.3	0.480
413°K:	6.0	4.7	0.200
	9.80	3.10	0.185
	14.60	2.80	0.270
	17.10	3.30	0.276
	20.3	5.3	0.480
500°K:	4.65	4.9	0.114
	7.20	4.00	0.230
	7.90	2.90	0.170
	9.30	4.30	0.210
	12.50	5.0	0.405
	19.0	3.20	0.370

* Reproducibility within ±2%.

DISCUSSION

I. THE MICROWAVE AND THE CONDENSED DISCHARGE SYSTEMS

The role of water vapour or hydrogen in increasing the production of atoms and ions in an electric discharge has not been explained completely. One explanation assumes that a layer of water vapour or hydrogen adsorbed on the wall of the discharge tube reduces the ability of the wall to catalyze atom recombination (152). In the present experiments with the microwave discharge in stable operation, a decrease in the N atom yield was noted within a few minutes after the liquid nitrogen trap was put on the system, or the H_2 flow was stopped. The speed with which the yield changed in this system suggests that the effect of H_2 or H_2O on the yield of atoms was not due solely to the gas adsorbed on the wall. On the other hand, a "poisoned" condensed discharge exhibited a long delay in approaching "unpoisoned" conditions when the impurity gas was removed, and this behaviour might be explained by slow desorption from the wall of the discharge tube.

It seems likely that traces of water or hydrogen are directly involved in the dissociation process, to increase the yield of atoms. This is indicated by the experimental observation that a lower voltage is capable of sustaining a condensed discharge in a "poisoned" than in an "unpoisoned" system. (This effect was not as marked in a microwave discharge.) Similarly, the breakdown potentials of oxygen and air have been found to be decreased in the presence of nitrogen oxides as contaminants (153). If the ionization potential of the impurity gas is lower than that of nitrogen, the number of electrons with energy greater than the ionization potential of the impurity gas, relative to the number of electrons with energy greater than the ionization potential of nitrogen, should increase with decrease in the applied potential. A lower voltage should then suffice to provide the electrons necessary to initiate and sustain the discharge. This might explain the lower voltage required to strike the discharge when H_2O was present, since it has a lower ionization potential than N_2. However, the similar effect with added H_2 cannot be so interpreted, since its ionization potential and that of N_2 are comparable.

As an alternative explanation for the effect of an impurity gas, it is suggested that a reduction in breakdown potential might be due to an interaction of energetic nitrogen species, N_2^*, with the impurity in the discharge zone. In pure nitrogen, a discharge current is the result of direct ionization by electron impact, $N_2 + e^- \longrightarrow N_2^+ + 2e^-$, but in the presence of an impurity of ionization potential lower than that of N_2, the following sequence conceivably might occur:

$$N_2 + e^- \longrightarrow N_2^* + e^-$$

$$N_2^* + M \longrightarrow N_2 + M^+ + e^-$$

where M is the impurity gas. The radiative life-time of N_2^* must be sufficient, of course, that collision of it with M is reasonably probable before radiation to a lower level occurs. This suggests, perhaps, that non-radiating metastables should be most susceptible to this process. By such a process, the same extent of positive ion formation might be maintained by electrons that have energy enough to create metastable N_2, but not N_2^+. A smaller discharge voltage might then suffice to initiate and maintain the discharge.

Spectroscopic studies (154) have indicated that when small amounts of oxygen, containing traces of H_2O, was added to a nitrogen stream before it entered the discharge tube, all the oxygen was adsorbed on the wall of the discharge tube and the hydrogen remained to catalyze the glow. This might explain, perhaps, the present observation that comparable amounts of water and hydrogen added to the nitrogen stream caused comparable enhancement of the afterglow emission.

To compare the microwave and the condensed discharges, it is necessary to consider the various factors that may contribute to generation of electrons, hence to ion formation in the two systems. In a condensed discharge through N_2, electrons could be generated by, (a) ionization with primary electrons; (b) secondary electron release after electron impact on gas atoms; (c) secondary emission after impact of electrons on the anode; or impact of positive ions on the cathode; (d) electron release due to the photoelectric effect. All of these may influence the number of electrons generated per electron released from the cathode under the applied potential. The last two factors cannot apply to microwave systems. Moreover, it seems likely that, for comparable experimental conditions, a "poisoned" microwave unit is less effective than a condensed discharge in producing electrons by factors (a) and (b).

As indicated previously, it is possible that the ion current in a discharge tube might be increased by ionization of impurity gas by N_2*. The much smaller effect of traces of H_2O or H_2 on the N atom yield in a microwave, than in a condensed discharge, might then reflect a lower capability for forming excited molecular nitrogen species in the microwave discharge. This would be in accord with the observations that active nitrogen from a condensed discharge is capable of promoting chemical changes that are not possible (or do not seem to occur significantly) with active nitrogen in a microwave system. Presumably the condensed discharge produces a higher concentration of excited molecular species capable of initiating such reactions. A power increase to a microwave discharge does result, however, in a more intense afterglow, with concomitant weakening of the First Positive bands (155), and this indicates that higher energy collisions of ions and electrons may yield a higher population of the C, rather than the B state of N_2 in such systems.

As with the microwave discharge so also the virtually continuous condensed discharge used in the present study approached "unpoisoned" conditions more rapidly than the more discontinuous discharge. This again points to a comparative insensitivity of the more continuous discharges to the presence of impurity gases. This behaviour would parallel a greater concentration of electrons in the ionization process (since the interval between ionization periods is decreased), hence a faster approach to constant N atom concentration after the removal of any perturbing influence, such as an impurity gas.

It seems that the N atom concentration probably depends on the discharge characteristics, the pressure and catalyst concentration. It is not possible as yet to isolate the catalytic effects of the added gases from their recombination-inhibiting effects, since the final N atom concentration may be strongly affected by both.

II. THE DECOMPOSITION OF AMMONIA AND SULPHUR DIOXIDE

Neither NH_3 nor SO_2 was decomposed significantly by active nitrogen from a microwave discharge, nor by that from an "unpoisoned" condensed discharge of comparable relatively low active nitrogen content. It is tempting, perhaps, to attribute these observations simply to a too low concentration of the active species in these systems. However, no decomposition of either SO_2 or NH_3 was observed with active nitrogen (flow rate 6 x 10^{-6} mole/sec) from a "poisoned" microwave system (Table VI), while about the same flow rate of active nitrogen from a "poisoned" condensed discharge did cause appreciable reaction (Table VIII). It would appear, therefore, that active nitrogen produced by the two methods might be qualitatively different. For example, the electrode system might produce significant concentrations of metastables (53), while low powered microwave discharges might tend to produce atoms and vibrationally excited molecules almost exclusively.

The point might be raised, perhaps, that the decomposition of sulphur dioxide by active nitrogen from a condensed discharge required the presence of a "poison" (e.g., a trace of hydrogen) in the N_2 that entered the discharge and that H atoms formed in the discharge might be responsible for initiating destruction of SO_2. This seems quite unlikely. The flow rates of H_2 used to "poison" the discharge were so small ($\sim 0.07 \times 10^{-6}$ mole/sec or less, of which only a fraction would be present as H atoms) that only an efficient chain reaction could cause significant SO_2 decomposition. Moreover, substitution of N_2 in the discharge by argon, with a trace of H_2 added as a "poison", did not result in detectable decomposition of SO_2 ($H + SO_2 \longrightarrow OH + SO$ is endothermic to the extent of 24 kcal/mole). The presence of active nitrogen was therefore essential to the decomposition process.

It might be noted also, as a point of interest, that a sequence of reactions such as

$$SO + H \longrightarrow OH + S$$

$$OH + SO_2 \longrightarrow SO_3 + H, \text{ etc.}$$

is about 20 kcal/mole endothermic, in each step, and may be ruled out. Reactions such as

$$H + SO_2^* \longrightarrow OH + SO$$

$$OH + SO_2^* \longrightarrow SO_3 + H$$

where SO_2* is an energized molecule, might be exothermic, but they must also have been insignificant, since their occurrence would have caused a discrepancy between destruction of SO_2 estimated by acid-base titration of total acidity (SO_2 + SO_3) and its destruction estimated by the iodine titration of residual SO_2. In fact, agreement with the two methods was very good.

The persistence of the yellow nitrogen afterglow during the NH_3 and SO_2 reactions, even for very high reactant flow rates, indicates that these reactions involve a species other than N atoms in the ^4S ground state, which is generally recognized as the most abundant chemically reactive species in both the microwave and the condensed discharge systems. This conclusion is supported by the observation previously reported for NH_3 (49) and now extended to SO_2, that addition of excess NH_3 or SO_2 to active nitrogen from a microwave discharge does not affect its ability to destroy nitric oxide. Moreover, the present observations established that addition of SO_2 to active nitrogen from a condensed discharge, in which appreciable destruction of SO_2 did occur, also did not decrease the ability of the active nitrogen to destroy NO. This may be interpreted to indicate that the nitrogen atom concentration was unaltered by the presence of SO_2. Destruction of NH_3 or SO_2 is then probably the consequence of energy transfer from an excited nitrogen molecule.

Such an excited species might be formed directly during the discharge process, or by recombination of nitrogen atoms between flashes in the discharge tube or after the gas leaves the discharge tube. The last possibility does not seem to apply to the present system, since no increase in SO_2 decomposition was observed when the effective reaction time was increased by a factor of 30% in the presence of excess SO_2. Similarly, when SO_2 was alternately introduced into the reaction vessel at two points separated by 20cm, and the reaction was then allowed to proceed with the same reaction time at constant active nitrogen flow rate, smaller decomposition of SO_2 was observed when it was introduced at the lower point. This, too, suggests that the reactive species involved in the decomposition of SO_2 is probably not formed to an appreciable extent by homogeneous recombination of nitrogen atoms as the gas passes through the reaction tube.

The practically constant extent of SO_2 destruction (within ± 10-15%) when the N atom flow rate was increased from 6.8 to 14.5 and then to 19×10^{-6} mole/sec (at constant total pressure) implies that, under these conditions at least, the flow rate of N_2^* leaving the discharge tube was essentially constant. This suggests negligible deactivation of N_2^* by N atoms, in marked disagreement with the results of Young and St. John (156) who observed an extremely rapid ($>10^{-11}$ cc/molec-sec) deactivation of this state by N atoms. However, they used an "unpoisoned" low-powered Tessla discharge at about 150 kc to obtain the active nitrogen, rather than a condensed discharge, and it is possible that this might account for the discrepancy.

To sustain the suggestion that N_2* may be formed largely in the intervals between flashes by recombination of N atoms in the discharge tube, it is necessary to account for the seemingly constant N_2* concentration (cf. constant SO_2 decomposition) for different N atom flow rates. It may be recalled that the different N atom flow rates were obtained at constant pressure by throttling the pump. As the flow rate of molecular nitrogen through the discharge is decreased, the residence time of N atoms in the discharge zone is increased, and it might be that a decrease (or increase) in N atom concentration is compensated by an increase (or decrease) in number of collisions between the nitrogen atoms to yield N_2*.

It is possible, however, that recombination of atoms is not the main source of N_2*, that they are formed directly by electron impact, and that the presence of a constant amount of "poison" in the nitrogen stream modifies the formation of N_2* molecules in such a way that their concentration is practically independent of the N atom concentration.

Since both ammonia and sulphur dioxide affected the yellow nitrogen afterglow in the same qualitative manner, and since both were decomposed to approximately the same extent by active nitrogen from a condensed discharge, it seems likely that the same species is responsible for the initial energy transfer to NH_3 or SO_2 to cause their subsequent decomposition. It was indicated (5, 157) that several energetic species of sufficient life-time may be detected at low concentration in the nitrogen afterglow region. When ammonia was added to this region, it quenched certain bands on the First Positive System more effectively than others, but even large additions, up to 7% of the gas present (51), did not reduce the atomic nitrogen concentration. On the other hand, smaller additions of NH_3 quenched, quite effectively, part of the intense CN emission from some hydrocarbon-active nitrogen flames.

While several reactive species, in various electronic states of nitrogen, may participate in the afterglow, it was little affected by the relatively low concentration of NH_3 that quenched the CN emission almost completely. This suggests that the concentrations of all the electronic states of N_2 that precede the afterglow emission, (i.e., $^5\Sigma_g^+$, $^3\Delta_u$, $C^3\Pi_u^-$, $B^3\Pi_g$) remain approximately constant in the presence of NH_3, and that they are not the initiators of the CN emission when hydrocarbon is added. If the $^5\Sigma_g^+$ were responsible for the energy transfer process to NH_3 or SO_2, it would have to do so in competition with two other processes - the dissociation of $^5\Sigma_g^+$ to ground state N atoms, and a non-radiative transition to the $B^3\Pi_g$ state. Similarly, transfer of energy from the $B^3\Pi_g$ state to the NH_3 or SO_2 would be in competition with an allowed radiative transition to the $A^3\Sigma_u^+$ state. The radiative lifetime of $B^3\Pi_g$ is in the microsecond range and is thus too short for collisions with either NH_3 or SO_2 to be highly probable.

Again, if the $^3\Delta_u$ state is responsible for the energy transfer, and if it lies above $B^3\Pi_g$, it should readily undergo collision-induced transition to the $B^3\Pi_g$ state, and its life-time should be quite short. On the other hand, if the $^3\Delta_u$ lies below the B state, the failure to detect a band system analogous to the Vegard-Kaplan bands of the A state would indicate that its life-time is considerably longer than that of the A state. In fact, the results of Kenty (158) suggest that its life-time is several seconds, even in the presence of deactivating species. (It might be noted, however, that attempts to observe its <u>absorption</u> spectrum were unsuccessful).

If none of the electronically excited states of N_2 above the A state seem to be plausible species for causing the decomposition of NH_3 or SO_2, there remain the possibilities that either the A state itself, or vibrationally excited ground state nitrogen molecules, $(X^1\Sigma_g^+)$, might be responsible.

There is considerable evidence that active nitrogen contains vibrationally excited ground state molecules in relatively large quantities beyond the discharge (159), with vibrational excitation up to 7.5 eV (160). In view of their inefficient collisional deactivation by N_2, they might be responsible for most of the observed chemical effects of active nitrogen that seem not to be due to N atoms. However, there is some evidence (161) that glass wool is effective in removing vibrationally excited ground state nitrogen molecules. The addition of glass wool in at least two experiments of the present study produced no significant change in the decomposition of SO_2. This probably means that vibrationally excited nitrogen molecules are not responsible for the decomposition of SO_2. An unlikely alternative is that vibrationally excited molecules were formed in relatively large concentrations past the glass wool plug. It will be recalled, also, that SO_2 was not decomposed by active nitrogen from a microwave discharge which is known to be rich in vibrationally excited N_2 molecules (159), while it was decomposed by comparable concentrations of active nitrogen from a condensed discharge. The experimental evidence suggests, therefore, that vibrationally excited N_2 molecules are not responsible for the decomposition of NH_3 or SO_2.

There remains the possibility that the first electronically excited level of the N_2 molecule, i.e., N_2 $(A^3\Sigma_u^+)$, is the species that causes decomposition of the NH_3 and SO_2. A recent mass spectrometric study (160) has indicated that active nitrogen (or an activated nitrogen stream) contains about 1.5% of electronically excited N_2 molecules, of which N_2 $(A^3\Sigma_u^+)$ constitutes the major part. Considerable evidence supports the view that the A state might be populated from a mixture of species that may be formed in the discharge, and that it has a relatively long life-time (76, 60). This state had been detected by absorption spectroscopy (162, 64) and its zero vibrational level is 142 kcal above the ground state (62). This energy is enough to break the S-O bond in SO_2 and the N-H bond in NH_3 (bond strengths of 127 and 103 kcal/mole, respectively). These several factors make the excited $N_2(A^3\Sigma_u^+)$ molecule a species to which the decomposition of SO_2 and NH_3 may be reasonably attributed.

The importance of spin conversation in determining the rates of processes has been pointed out by Walsh (163) and discussed for active nitrogen systems by Evans and Winkler (4). In general, those processes are favoured in which total spin is conserved. If a process of the type

$$N_2(A^3\Sigma_u^+) + SO_2(A^1\Sigma_1) \longrightarrow N_2(\text{singlet}) + SO_2(\text{triplet})$$

were to occur, total spin would be conserved, and the SO_2 triplet should be lower lying than the N_2 triplet (164). While the first electronically excited level of SO_2 is a triplet state, with excitation energy of 74 kcal/mole above the ground state (165), it is not yet known whether a triplet state capable of leading to dissociation (D(SO-O)=127 kcal/mole) exists for this molecule.

If SO_2^* is not a triplet state, there might be sufficient perturbation of the excited state by higher lying levels that spin conservation becomes less important. The increasingly inhomogeneous magnetic effects due to heavy atoms is known to make the spin conservation rule less demanding. A similar effect might be introduced by the paramagnetic field of the unpaired electrons of oxygen (166) in SO_2 that would reduce the importance of spin conservation in its quenching of N_2^*.

If a triplet state appropriate to dissociation of SO_2 is assumed, the energy transfer from $N_2(A^3\Sigma_u^+)$ should be possible, particularly if there is a large overlap of the emission spectrum of N_2 $(A^3\Sigma_u^+)$ with the absorption spectrum of SO_2, and if both radiative transitions are highly probable (164). On the other hand, although total spin would be maintained, the transition from the triplet A state of N_2 to the ground state, N_2 $(X^1\Sigma_g^+)$, is not allowed. The coupling between these two states of nitrogen would be weak and the process would have correspondingly low probability. One factor, however, that might favour energy transfer in such a process is a relatively long life-time of the energy donor. Obviously, the life-time of an appropriate SO_2^* is not known, since it has not yet been identified. If it were assumed to be a $(^3\Sigma)$ state, a relatively short life-time of about 0.0005 sec might be associated with it (167). (Any disagreement between calculated and measured life-time of SO_2^*, if it does arise, could be ascribed, perhaps, to differences in the configuration of SO_2 in the ground and in the excited state). On the other hand, while there is still some question about the life-time of the A state of N_2, it appears to be in the neighborhood of one second. Such relatively long life-time should increase the probability of spatial overlap between the two states, hence the probability of energy transfer.

In the present study, the addition of NH_3 or SO_2 to an active nitrogen stream indicated a slight but perceptible partial quenching of the yellow afterglow (presumably due to partial quenching of the First Positive System). Moderately high vibrational levels of the N_2 $(A^3\Sigma_u^+)$ state correspond to lower vibrational levels of the B state. It appears likely, therefore, that N_2 molecules formed in high vibrational levels of the A state, in the absence of NH_3 or SO_2, may undergo a collisionally-induced transition to the B state, from which they may radiate back to the A state, or be collisionally quenched to the vibrationally excited ground state. Further evidence that nitrogen molecules may cross from the A state to the B state can be deduced from the observation (34) that the vibrational energy distribution of the $B^3\Pi_g$ emission in the $^{14}N_2$ and $^{15}N_2$ afterglows are identical at higher, but differ at lower energies. Emission from lower levels was more intense with $^{14}N_2$ than with $^{15}N_2$, presumably because the levels of the former were better matched to those in the A state. The fact that NH_3 quenched transitions from lower levels of the B state more efficiently than transitions from higher levels, suggests that NH_3, and possibly also SO_2, may inhibit the collision-induced population of the lower levels of the B state from the A state by deactivating the latter. An interesting experiment would thus be to introduce SO_2 into an active nitrogen stream and determine whether it shifts the intensity distribution maximum of the First Positive System to higher vibrational levels of the B state.*

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*If processes other than radiation remove the A state, i.e., reactions with N atoms (156), and vibrationally excited ground state N_2 molecules were responsible for the decomposition of NH_3 and SO_2, this would require that the partial quenching of the First Positive System in the presence of NH_3 or SO_2 may be attributed to the deactivation of the vibrationally excited N_2 molecules. However, there is no appropriate energy matching between the ground state and the B state to facilitate collision induced population of the B state from vibrationally excited ground state N_2 molecules.

If there is a resonant match between the partners undergoing collision of the second kind (NH_3 or SO_2 colliding with an electronically excited N_2 molecule), presumably very little electronic energy would be converted into kinetic energy of translation, and the energy acceptors (NH_3 or SO_2) would be raised to an excited state. If the excitation energy of the donor (N_2 ($A^3\Sigma_u^+$)) is larger than the thermochemical energy of dissociation of NH_3 or SO_2, these may be raised to a repulsive state such that dissociation would ensue within the time of one vibration. The decomposition of SO_2, initiated by N_2 ($A^3\Sigma_u^+$), may well follow such a course. The products would presumably be SO +O, since dissociation to S + O_2 would involve the rupture of two bonds, and require more energy than that available from N_2 ($A^3\Sigma_u^+$). This conclusion is supported by the observation that shock heated SO_2 (168) gave a <u>true</u> absorption continuum, with a limit at 125 kcal/mole for SO and O atoms in the ground state. This may suggest that if the reaction $SO_2 \rightarrow S + O_2$ were energetically possible under these conditions, rearrangement occurred in the excited state (perhaps to S-O-O), and the <u>diffuse</u> spectrum resulted from crossing of potential curves.

The formation of SO and O atoms was also predominant in a weak discharge through an SO_2/Ar mixture (169). The production of an SO_2 afterglow was observed, the intensity of which was proportional to [SO] and [O]. Again, it has been found that no ozone is formed from the SO_2 discharge (170), in contrast to the NO_2 and CO_2 discharges in which ozone was found. A probable explanation is that the reaction $SO + O + M \rightarrow SO_2 + M$ is of major importance during the process.

If the A state of nitrogen causes direct decomposition of SO_2 to SO and oxygen atoms, it is likely that the products will be in their ground states. The formation of an excited O atom, for instance, would increase the energy of dissociation by an amount equal to the excitation energy associated with the oxygen atom. To form O (^1D), the lowest-lying excited state for the oxygen atom, the energy requirement would be about 170 kcal/mole (168), a quantity in excess of that associated with the N_2 $(A^3\Sigma_u^+)$ state. It is interesting, perhaps, that no excitation of the CN radical was observed when it was formed in the reactions of $(CN)_2$ or HCN with active nitrogen (62), presumably because of the energy requirement in excess of that in N_2 $(A^3\Sigma_u^+)$.

III. REACTIONS OF NO AND HYDROCARBONS WITH ACTIVE NITROGEN IN THE PRESENCE OF AMMONIA AND SULPHUR DIOXIDE

The relative effects of NH_3 and SO_2 on the very fast reaction of active nitrogen with NO appear, at first sight, not to be comparable. Nevertheless, they do permit some estimate of the relative rates of the reactions of NH_3 and SO_2 with active nitrogen. The continuous drop in the NO titration value as the mole fraction of NH_3 was increased implies at least some reaction of N atoms, perhaps with the decomposition products of NH_3[ϕ]. If the NO titration

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[ϕ] The destruction of NO by the decomposition products of NH_3 is ruled out, since NO flow was never in excess of the active nitrogen flow rate.

curve (Fig. 7) may be taken to be valid in the relatively high NH_3 or SO_2 flow rate range (above 70 x 10^{-6} mole/sec), the virtual plateau attained indicates the maximum extent of NH_3 decomposition. However, the relatively high flow rate of NH_3 necessary to attain this limiting value, compared with the much lower NH_3 input required to reach a decomposition plateau in the absence of NO (Table VIII), strongly suggests that deactivation of the A state by NO is rapid. This view has recently been confirmed (171).

A practically constant NO titration endpoint was obtained when a mixture of SO_2 and NO was admitted to an active nitrogen stream, and apparently little decomposition of SO_2 occurred. Had it done so at an appreciable rate to form SO, which reacts very rapidly with N atoms (see later), the SO would have competed with NO for the nitrogen atoms, and the net result would have been comparable with the reaction in the presence of NH_3. The delayed decrease in the NO titration (for SO_2 flow rates below 70 x 10^{-6} mole/sec) indicates that the efficiency of NH_3 in quenching the A state of nitrogen is greater than that of SO_2, while the delayed appearance of a plateau in the presence of SO_2 might indicate a relatively slower reaction of SO_2 with active nitrogen.

The observation that HCN production from methane, ethane, and cyclopropane was suppressed in the presence of ammonia or sulphur dioxide suggests that the reactive species removed by NH_3 or SO_2 initiates a reaction that ultimately leads to HCN production. This is in accord with the conclusions of a previous study (87) with the methane and ethane reactions;

in both cases, the A state was assumed to be the initiating species. That HCN production was suppressed to about the same extent by NH_3 and SO_2 in each of these reactions probably means that there was not much further attack of the hydrocarbon by the decomposition products of NH_3 or SO_2 (e.g., H atoms and O atoms, respectively) to facilitate HCN production at room temperature. However, it seems likely that the relatively higher efficiency of NH_3 in inhibiting HCN formation from CH_4 than from C_2H_6 is associated with the more facile attack of ethane by H atoms than by O atoms*. It may also indicate that H atoms attack ethane more readily than methane. The addition of H atoms has been shown to increase the HCN yield from the active nitrogen - C_2H_6 reaction at elevated temperatures (81).

The more effective suppression by SO_2 than by NH_3 of the HCN yield from cyclopropane probably also implies that H atoms from the decomposition of ammonia attack this hydrocarbon more readily than do O atoms. Furthermore, it seems very probable that this reaction is also initiated by collisions with electronically excited nitrogen molecules, as are those of the straight-chain paraffins, CH_4 and C_2H_6.

Increased production of HCN from a hydrocarbon, in the presence of NH_3, is readily explained if the primary attack of the hydrocarbon molecule, RH, by N_2 $(A^3\Sigma_u^+)$ yields a radical R•, and an H atom which subsequently attacks the hydrocarbon to

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*The methane and ethane reactions with H atoms are associated with activation energies of 7.4 and 6.8 kcal/mole, respectively (172, 173). The corresponding activation energies for the O atom reactions are 8.7 and 7.5 kcal/mole, respectively (174, 175).

produce a radical* that is readily attacked by N atom. (Removal of the radicals by the parent hydrocarbon is slow (177) by comparison with the N atom reaction, and may be ignored in these investigations.)

Although the CN chemiluminescence was quenched during these reactions by addition of rather specific amounts of NH_3 or SO_2, production of HCN was never completely suppressed. The extent to which the HCN yield was reduced tended to become constant at high hydrocarbon flow rates; this was particularly evident for the methane reaction, in which the inhibited HCN production attained a virtual plateau value. The behaviour suggests the occurrence of a residual reaction of the hydrocarbon with another species to form HCN. If the reaction $CH_4 + NH_3 \rightleftarrows HCN + 3H_2$ were responsible for preventing complete suppression of HCN production from CH_4 in the presence of NH_3, the high flow rates of SO_2 used should have reduced the HCN yield to practically zero, and this did not occur. (It might be noted, also, that equilibrium for this reaction at room temperature lies far to the left (178)). It seems, therefore, that some species, not removed by NH_3 or SO_2, such as N atoms, is responsible for the observed residual HCN production. A lower efficiency of SO_2, relative to NH_3, for quenching electronically excited N_2, could explain the observation that the HCN yield representing this residual reaction is approached at relatively higher SO_2 than NH_3 flow rates.

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*With cyclopropane, the radical is probably not trimethylene, since recyclization is many times faster than ring rupture in energized cyclopropane (176).

Since CN emission is almost completely quenched in these reactions, while HCN production continues, there would seem to be little relation between the intensity of the emission and the formation of HCN. Excitation of the CN spectrum might, for example, result from a termolecular reaction involving N atoms, while HCN might be formed in a bimolecular process. The rate of HCN formation may therefore be considerably higher than the rate of formation of excited CN radicals.

Of special interest was the reaction of ethylene with active nitrogen. In this reaction, HCN production was accentuated by addition of NH_3 or SO_2, except with relatively low ammonia flow rates (Fig. 8) for which a slight decrease in the HCN production was observed. This decrease might be associated with a partial removal of N atoms by the decomposition products of NH_3, or with removal of N_2 $(A\,^3\Sigma_u^+)$ by NH_3. The latter explanation would imply that part of the HCN production is dependent upon attack of C_2H_4 by excited nitrogen molecules. There is perhaps no reason to suppose that this should not occur. If it did, and H atoms were formed, they should react rapidly with C_2H_4 to form radicals (e.g., C_2H_5) which would be rapidly attacked by N atoms to form HCN. The same should be true for H atoms formed during the decomposition of NH_3. In either case a chain mechanism is possible, of the type

$$C_2H_4 + N_2\ (A\,^3\Sigma_u^+) \rightarrow C_2H_4^* \rightarrow C_2H_3\cdot + H \quad ..... (1)$$

$$\xrightarrow{N} HCN + CH_3. \quad ..... (2)$$

$$CH_3\cdot + N \rightarrow HCN + 2H \quad ..... (3)$$

$$H + C_2H_4 \rightarrow C_2H_5\cdot \quad ..... (4)$$

$$C_2H_5\cdot + N \rightarrow HCN + CH_3\cdot + H.. \quad (5)$$

Since reaction (4) has a rate constant larger than that for the initial N atom attack on ethylene (179), and since H atom production is extensively maintained by reactions (3) and (5), a possible competition between reaction (4) and reaction (1) is expected to occur. This competition might be responsible for the promotion of HCN yield above the plateau value from the reaction of ethylene with active nitrogen in the absence of NH_3 or SO_2, since it might well be that C_2H_5 and CH_3 radicals would be better titrants of N atoms than ethylene itself.

It is not likely that HCN is produced significantly by attack of CH radicals on NH_3, when NH_3 is added to the C_2H_4-active nitrogen reaction, in the manner that has been assumed for the corresponding reaction with acetylene (180). It has been observed experimentally that the intensity of CH bands in the C_2H_4-active nitrogen system is three orders of magnitude lower than in the C_2H_2-active nitrogen system (181). Neither is any significant HCN formation expected to result from the reaction of NH_3 with ethylene. Attempts in the present study to quench the NH_3-active nitrogen reaction by the addition of C_2H_4 always resulted in a decrease in the decomposition of NH_3. This implies that neither C_2H_4, nor its decomposition products were capable of entering into reaction with NH_3.

The production of HCN from C_2H_4 in the presence of NH_3 should eventually level off when the maximum consumption of N atoms has been attained. In fact, this curve approaches an HCN level comparable with that of the NO titration value, presumably because of the beneficial effect of H atoms on HCN production. This behaviour suggests that the maximum HCN yield from ethylene alone is not a true measure of the nitrogen atom content.

There was no decrease in the HCN production from C_2H_4 in the presence of relatively low SO_2 flow rates, as there was for relatively low NH_3 additions. This might reflect a lower efficiency of SO_2 than NH_3 for quenching excited nitrogen molecules, but it might also suggest a chain mechanism initiated by O atoms from the decomposition of SO_2. The reactivity of H atoms and O atoms toward C_2H_4 is about the same (182), and either might be invoked as chain carriers:

$$SO_2 + N_2\ (A^3\Sigma_u^+) \longrightarrow N_2\ (X^1\Sigma_g^+) + SO_2^* \begin{array}{l} \nearrow SO + O \\ \overset{N}{\searrow} SO,\ NO,\ O,\ S,\ etc... \end{array} \quad (6)$$

$$SO + N \longrightarrow NO + S \quad ..... \ (7)$$

$$NO + N \longrightarrow N_2 + O \quad ..... \ (8)$$

$$O + C_2H_4 \longrightarrow CHO\cdot + CH_3\cdot \quad ..... \ (9)$$

$$CHO\cdot + N \longrightarrow HCN + O \quad .....(10)$$

$$CH_3\cdot + N \longrightarrow HCN + 2H \quad ..... \ (3)$$

$$C_2H_4 + H \longrightarrow C_2H_5\cdot \quad ..... \ (4)$$

$$C_2H_5\cdot + N \longrightarrow HCN + CH_3\cdot + H \quad ... \ (5)$$

Reaction (9), which initiates an O atom chain, can proceed only after the initial decomposition of SO_2 has occurred by reaction (6). The intermediate formation of CHO· radicals in the reaction of C_2H_4 with O atoms has been detected (181), and their fast reaction with N atoms is a reasonable assumption. Reactions (7) and (8) are now known to be very fast, and their removal of N atoms might be expected to decrease the HCN production from C_2H_4 in the presence of SO_2. However, a possible decrease in HCN yield might be offset, partially or completely, by the rapid formation of HCN from the alkyl radicals that are produced in the chain reaction. Experimentally, the HCN yield in the presence of SO_2 approaches a plateau value that is lower than the NO titration value (15.7×10^{-6} mole/sec), in contrast to the behaviour with NH_3. Apparently a relatively large number of N atoms are consumed in the presence of SO_2 without the production of HCN. This could be accounted for by reactions (7) and (8), coupled perhaps with some nitrogen sulphide formation.

The reactions of propane and n-butane with active nitrogen, in the presence of NH_3 or SO_2, show features similar to those outlined for the corresponding systems with methane and ethane, including the effect of their decomposition products during the reactions. The initial inhibition in the HCN production from propane and n-butane was always more pronounced in the presence of SO_2 than in the presence of an equal flow rate of NH_3. At higher hydrocarbon levels, NH_3 promoted the HCN yield to a greater extent than did SO_2. This is in accord with the relative effects of the secondary attack of the hydrocarbon by H atoms and O atoms from the decomposition of NH_3 and SO_2, respectively*. Propyl and butyl radicals, formed in the presence of H atoms from NH_3, may subsequently be attacked by N atoms to form HCN and induce

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*It is rather difficult to treat quantitatively the efficiencies of NH_3 and SO_2 in suppressing or promoting HCN production, since the reactions are not simple competitive reactions, and would not conform to a simple kinetic treatment.

a chain reaction which will further promote the HCN yield. Similarly, a carbonyl compound may be formed by O atom reaction in the presence of SO_2. The H and O atom attack on the parent hydrocarbon would be at about equal rates (183, 184), while attack of N atoms on the carbonyl compound might well be slower than attack on the propyl or butyl radical. This could account for the negligible promotion of HCN production in the presence of SO_2. In a current investigation of HCHO reaction with active nitrogen, in this laboratory, relatively little HCN appears to be formed (185).

IV. THE REACTION OF SULPHUR DIOXIDE WITH ACTIVE NITROGEN

1. MECHANISM OF THE REACTION

As seen previously, both the NH_3 and SO_2 reactions with active nitrogen appear to be induced by energy transfer from excited nitrogen molecules. Unlike the NH_3 reaction, the limiting extent of SO_2 decomposition passes through a flat maximum with increase of reactant flow rate (Fig. 15). Moreover, there was a practically constant extent of the SO_2 reaction in the pressure range 2 to 3 torr, for a particular SO_2 flow rate. The experimental behaviour suggests that the SO_2-active nitrogen system might involve processes superimposed on the decomposition of the energized SO_2 molecule, of a type not operative in the NH_3 reaction, and that SO_2 itself might be responsible for these processes. These observations, together with the nature of the reaction products, suggest that the following sequence of reactions seem to merit consideration in the SO_2-active nitrogen system:

$SO_2 + N_2^* \rightarrow SO_2^* + N_2$ ..... (1)

$SO_2^* \rightarrow SO + O$ ..... (2)

$SO_2^* + N \rightarrow SO + NO$ ..... (3)

$SO_2^* + SO_2 \rightarrow SO_2 + SO_2$ ..... (4)

$NO + N \rightarrow N_2 + O;$ $\Delta H = -75$ kcal/mole ..... (5)

$SO + N \rightarrow NO + S;$ $\Delta H = -30$ kcal/mole ..... (6)

$SO + O \rightarrow O_2 + S;$ $\Delta H = 2$ kcal/mole ..... (7)

$SO + O + M \rightarrow SO_2 + M;$ $\Delta H = -127$ kcal/mole ..... (8)

$SO + SO \rightarrow SO_2 + S;$ $\Delta H = - 8$ kcal/mole ..... (9)

$\rightarrow S_2 + O_2;$ $\Delta H = 20$ kcal/mole .....(10)

$S + N + M \rightarrow$ (S-N Stable products) .....(11)

$SO_2 + O \rightarrow SO + O_2;$ $\Delta H = 10$ kcal/mole .....(12)

$SO_2 + O + M \rightarrow SO_3 + M;$ $\Delta H = -83$ kcal/mole .....(13)

$SO_3 + O \rightarrow SO_2 + O_2;$ $\Delta H = -34$ kcal/mole .....(14)

$SO_3 + N \rightarrow SO_2 + NO;$ $\Delta H = -66$ kcal/mole .....(15)

Any oxygen atoms formed during the course of the overall reactions that occur are probably removed mainly by recombination at the wall of the vessel. Their removal by reactions (7) and (12) is improbable, since both are about 2 and 10 kcal/mole endothermic, respectively. It is true that participation of excited (^1D) oxygen atoms would make these reactions exothermic. However, not only is it unlikely that excited oxygen atoms would be formed, but they would be rapidly deactivated by molecular nitrogen, with a rate constant larger even than that of the very fast NO + N reaction (186). Although reaction (13) is exothermic

(~80 kcal/mole), it is third order, and its contribution should be small. This is supported by the experimental observation, mentioned previously, that formation of SO_3 is slow. Reaction (8) is also exothermic (127 kcal/mole), but it, too, is third order and would be too slow to remove significant amounts of O atoms; moreover, the concentration of SO would be low, owing to its rapid reaction with nitrogen atoms (see "The reaction of SO with atomic nitrogen").

Reaction (9) would probably be insignificant in competition with the fast reaction of SO with N atoms; moreover, it appears to be a relatively slow reaction, since no disproportionation of SO was detectable under conditions of the present experiments. Removal of SO by reaction (10) is also unlikely owing to its apparent endothermicity. A rapid consumption of SO by nitrogen atoms to yield elemental sulphur would be followed by the relatively slow reaction (11).

Reactions (14) and (15) would be limited in extent, not only by the relatively insignificant formation of SO_3 in this system, but by their own inherent slowness (see later).

Reactions (1) to (6) remain to be considered as those that are likely to be most extensively involved in the SO_2-active nitrogen reaction.

There seems to be little doubt from the experimental behaviour, and the interpretation of it outlined previously, that reaction (1) is the primary process in the reaction of active nitrogen with SO_2. The relative significance of reactions (2), (3) and (4) probably can be discussed most advantageously by considering the kinetics of the system.

2. KINETICS OF THE REACTION

If it is assumed that reaction (1) is faster than either reactions (2) or (3), so that one or other of these is rate controlling, SO_2^* would be produced faster than it would undergo reaction. Hence, deactivation of SO_2^* would have to occur rapidly by

$$N_2 + SO_2^* \longrightarrow N_2^* + SO_2$$

or perhaps even more rapidly by

$$SO_2 + SO_2^* \longrightarrow SO_2 + SO_2$$

This would seem to imply that reaction (4) and reaction (1) would have roughly comparable rates, and most of the N_2^* species would be lost with little or no decomposition of SO_2. This is contrary to the experimental behaviour. Alternatively, the energy transfer from N_2^* to SO_2 may be relatively slow, and rate-controlling in the overall decomposition of SO_2 by active nitrogen.

On the assumption that the energy transfer, reaction (1), is rate-controlling, the initial flow rate of the A state molecules (at jet, J_2) responsible for the reaction, should be given approximately by the limiting extent of destruction of SO_2 (or NH_3) that is attained with complete reaction in the presence of excess reactant (Fig. 15). Using this value for N_2^*, second order overall rate constants were calculated for the SO_2 decomposition by active nitrogen. The excited SO_2 molecule formed, SO_2^*, is assumed to disappear relatively fast by subsequent spontaneous decomposition, or by the attack of nitrogen atoms. The results, given in Table

XXV yielded consistently lower reaction rate constants for higher initial flow rates of SO_2. Since this effect was virtually independent of total pressure (between 2-3 torr), it appeared that it was due solely to the change in SO_2 flow rate in this pressure range, which in turn, suggested that it resulted from the self-deactivation process

$$SO_2^* + SO_2 \longrightarrow SO_2 + SO_2$$

Indirect support for the occurrence of such a process might be derived from the observation that the intensity of fluorescence from lower excited states of SO_2 (the first triplet and second singlet) decreased with increase of SO_2 pressure (167). This suggested an efficient self-quenching process. On the other hand, hydrogen and oxygen were very poor quenchers, and this gives support to the observation in the present study that increased partial pressure of nitrogen did not cause a detectable change in the extent of SO_2 decomposition. (Dipole interactions are presumably responsible for coupling between two molecules to exchange energy, and the van der Waals attraction is probably much stronger between SO_2 molecules than between SO_2 and N_2 molecules.)

The probability that SO_2 should decompose spontaneously, reaction (2), relative to the probability that it be destroyed by nitrogen atoms, reaction (3), clearly depends upon the unknown life-time of the excited SO_2 species. It appears from the change in the overall rate constants with SO_2 flow rate that both these processes might occur simultaneously.

If reactions (1), (2) and (4) are considered, and the removal of SO_2^* by N atoms is excluded, the destruction of SO_2 by active nitrogen (assuming steady state treatment for SO_2^*) takes the form

$$-d[SO_2]/dt = k_1[SO_2]\,[N_2^*] - \frac{k_1k_4\,[SO_2]^2\,[N_2^*]}{k_2 + k_4\,[SO_2]}$$

$$= \frac{k_1\,[SO_2]\,[N_2^*]}{1 + k_4\,[SO_2]/k_2} \qquad \ldots\ldots (1)$$

Since k_2 and k_4 represent first and second order rate constants, respectively, and $[SO_2] \approx 10^{15}$ molec/cc,

$$k_4\,[SO_2]/k_2 \gg 1$$

The decomposition of SO_2 would then be entirely independent of SO_2 input in the flow rate range 3 to 20 x 10^{-6} mole/sec. This is in sharp contradiction to the experimental evidence, and the reaction sequence leading to equation (1) may be rejected.

If reactions (1), (3) and (4) are assumed to occur, with reaction (1) as the rate controlling step, the disappearance of SO_2 may be expressed by

$$-d[SO_2]/dt = k_1\,[SO_2]\,[N_2^*] - \frac{k_1k_4\,[SO_2]^2\,[N_2^*]}{k_3[N] + k_4\,[SO_2]}$$

$$= \frac{k_1\,[SO_2]\,[N_2^*]}{1 + k_4\,[SO_2]/k_3[N]} \qquad \ldots\ldots (2)$$

On the other hand, if the spontaneous decomposition of SO_2^*, reaction (2), is also included in the kinetic scheme, a similar treatment gives

$$-d[SO_2]/dt = k_1 [SO_2][N_2^*] - \frac{k_1k_4[SO_2]^2[N_2^*]/k_3[N]}{1 + k_2/k_3[N] + k_4[SO_2]/k_3[N]}$$

$$= \frac{k_1 [SO_2][N_2^*](1 + k_2/k_3[N])}{1 + k_2/k_3[N] + k_4[SO_2]/k_3[N]} \qquad .....(3)$$

For experimental conditions such that

$$1 \gg k_2/k_3[N]$$

the rate expressions (2) and (3) become equivalent. Such conditions may be reasonably assumed for the present study, since $[N] \approx 10^{15}$ molec/cc and k_2/k_3 should be larger than unity but appreciably smaller than 10^{15}.

If k_1' represents the overall rate 'constant' for the SO_2 decomposition by active nitrogen, where

$$k_1' = \frac{k_1}{1 + k_4[SO_2]/k_3[N]}$$

the rate of disappearance of SO_2 becomes a function of the ratio $[SO_2]/[N]$. In fact, this concentration ratio will determine whether k_1' (which is not a constant) might be identified with the rate constant k_1, for the energy transfer process. At sufficiently low flow rates of SO_2 relative to the N atom flow rate, $1 > k_4[SO_2]/k_3[N]$, and $k_1' \sim k_1$; at SO_2 flow rates almost equal to, or greater than the available N atom flow rate $k_1' < k_1$.

With the present experimental conditions, the N atom flow rate was about 20×10^{-6} mole/sec, and the calculated rate constants were about 5 times smaller for higher, than for lower SO_2 flow rates (Table XXV).

TABLE XXV

Overall Rate Constants** for the Reaction of Sulphur Dioxide with Active Nitrogen

Total pressure 2 torr
Temperature 333°K
(Results based on data in Table XVIII)

SO_2 input (mole/sec)x10^6	Reaction time (msec)	N_2* flow*** (mole/sec)x10^6	$k_1' \times 10^{15}$ (cc/molec-sec)
4.53	313	1.00	2.7
4.74	291	1.00	2.3
5.01	306	1.00	2.6
5.19	330	1.00	2.9
6.08	274	1.00	2.1
6.84	265	1.00	1.8
7.35	270	1.00	1.9
8.45	199	1.00	1.2
9.39	259	1.00	1.6
10.03	147	1.00	1.0
10.25	208	1.00	1.1
13.02	200	1.00	0.9
17.29	168	0.95	0.7
20.0	144	0.90	0.6
22.3	157	0.90	0.6

**Calculated from

$$k_1' = \frac{\ln([SO_2]_o/[SO_2]_t)}{[N_2^*]_o - [SO_2]_o + [SO_2]_t}$$

which was obtained upon integration of the rate expression developed on the assumption that the decomposition of SO_2 was initiated by excited nitrogen molecules, where

$[SO_2]_o$, $[SO_2]_t$ = concentration of SO_2 initially, and at time t, respectively

***$[N_2^*]$ = initial concentration of excited N_2 molecules estimated from plateau concentration of SO_2 decomposition (Fig. 15) to within ± 2-10%, with a corresponding standard error of ± 20-25% in k_1'.

If, now, the reciprocal of the left hand side of expression (2), i.e., $-\left(\frac{d[SO_2]}{dt}\right)^{-1}$, is plotted against the reciprocal of the SO_2 concentration, a linear relation is obtained (Fig. 18, based on data in Table XXVI). The value of k_4/k_3, from the intercept and the slope of the line, is approximately 10, which suggests a value of about 7×10^{-15} cc/molec-sec for k_1 at 333° K.

TABLE XXVI

Reaction of Sulphur Dioxide with Active Nitrogen

Data for Evaluation of the Ratio k_4/k_3

Reaction time (msec)	SO_2 input (mole/sec)x10^6	SO_2 recovered (mole/sec)x10^6	$k_1' \times 10^{15}$ (cc/molec-sec)
313	4.53	3.91	2.7
306	5.01	4.38	2.6
330	5.19	4.51	2.9
265	6.84	6.26	1.8
199	8.45	7.97	1.2
259	9.39	8.76	1.6
147	10.03	9.63	1.0
144	20.0	19.6	0.6

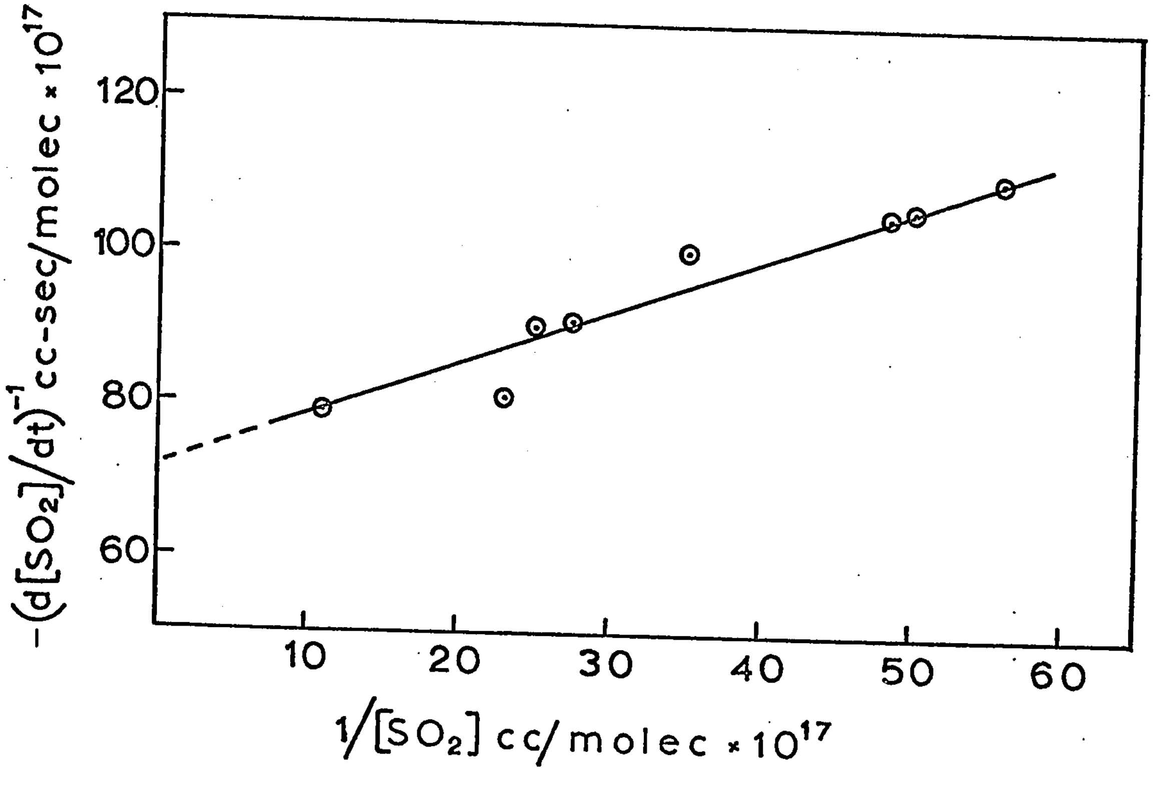
The relatively inefficient energy transfer from N_2^* to SO_2, (reaction 1), suggests that a fairly low steric factor might be involved in the process, since a relatively low activation energy (~2 kcal/mole**) was associated with the reaction in the temperature range 333 to 688°K. (Table XXVII and Fig. 19).

**An error of ±20% in k_1' will result in a negligible error in log k_1', so that the main error in the activation energy will be due to the error in the temperature measurement, i.e., at least of the order of ±15%.

Figure 18

Date for the evaluation of the ratio k_4/k_3

Plot of $-1/(d[SO_2]/dt)$ vs $1/[SO_2]$



$-(d[SO_2]/dt)^{-1}$ cc-sec/molec × 10^{17}
120
100
80
60
10
20
30
40
50
60
$1/[SO_2]$ cc/molec × 10^{17}

TABLE XXVII

Overall Rate Constants for the Reaction of Sulphur Dioxide with Active Nitrogen at Elevated Temperatures

N_2* flow rate 1.00 x 10^{-6} mole/sec
(Results based on data in Table XIX)

	SO_2 input (mole/sec)x10^6	Reaction time (msec)	k_1' (cc/molec-sec)x10^{14}
473°K:	4.52	30	0.7
	4.55	121	0.7
	4.61	288	0.7
	4.63	52	0.7
543°K:	4.52	121	0.8
	4.55	52	0.9
	4.61	320	0.8
	4.63	35	0.8
688°K:	4.53	24	1.4
	4.53	187	1.5
	4.57	233	1.4
	4.62	40	1.4
	4.65	90	1.5

TABLE XXVIII

Reaction of Sulphur Dioxide with Active Nitrogen

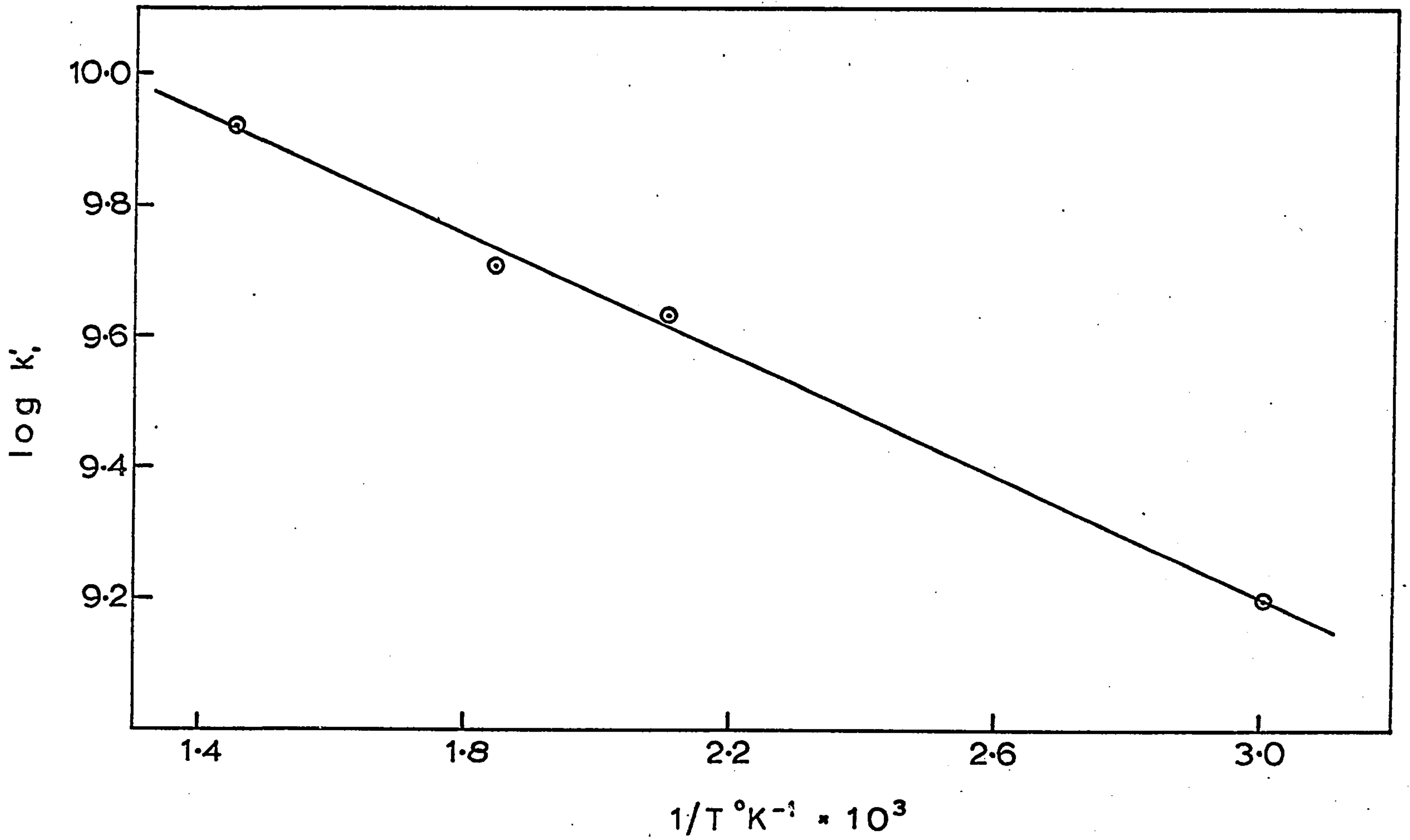
Temperature Dependence

k_1' (cc/mole-sec)x10^{-9}	T (°K)
1.6	333
4	473
5	543
8	688

Figure 19

Arrhenius Plot for the reaction

of SO_2 with Active Nitrogen


10·0
9·8
9·6
9·4
9·2
log K'₁
1·4
1·8
2·2
2·6
3·0
1/T °K⁻¹ × 10³

Energy transfer reactions do not exhibit a strong temperature dependence (187), and since vibration-to-vibration transfer tends to become less efficient at higher temperature (188), self-quenching of SO_2 becomes less important, i.e., a smaller fraction of energized SO_2 molecules becomes deactivated. As a result, a small net increase in the decomposition of SO_2 is observed with increasing temperature.

The temperature effect, which is given by the Arrhenius relation, can be expressed in the form

$$\ln k = \ln A - E_a/RT$$

so that the frequency factor A, could be obtained from the intercept in Fig. 19. This yields a value $A = 10^{10.6}$cc/mole-sec. If the kinetic collision number for a bimolecular reaction is taken as 7×10^{-10}cc/molec-sec (189), a steric factor of $2.1\text{x}10^{-4.4}$ is obtained for the reaction. This implies that the collision efficiency for the reaction is low, and that the energy transfer probably does not involve resonance. On the other hand, although it might be true that the efficiency of an energy transfer could be explained in terms of vibrational structure, it is presumably not the sole determining factor in these processes. For example, rotational effects during collisions might be significant; appreciable rotation of the energy acceptor toward the optimum orientation during a collision might increase the probability for the process. However, the low steric factor may also reflect a spin disallowed energy exchange between N_2* and SO_2.

There seem to be no data that enable the energy transfer in the active nitrogen - SO_2 system to be compared with the behaviour of other systems. Since energy transfer is closely associated with fluorescent and quenching phenomena, relevant data on these matters are obviously indispensable for such a comparison. However, most of the spectroscopic data available at present are related to excitation energies of SO_2 up to about 100 kcal/mole, which is below the dissociation limit of SO_2. The observed effects at these energies, therefore, are not directly applicable to the present system, in which a larger excitation energy may be involved, notwithstanding the uncertainties associated with the origin of the SO_2 emission.

A number of excited molecules of SO_2 have been postulated, with their corresponding electronic states, but there is no real evidence that a particular excited state of SO_2 is responsible for a particular process. A study of the SO_2 spectrum with high resolution is desirable.

V. THE REACTION OF SULPHUR MONOXIDE WITH ATOMIC NITROGEN

The relatively long duration, and relatively intense emission of the SO_2 afterglow observed in the oxidation of CS_2 vapour and H_2S gas (190) have been interpreted to indicate that sulphur monoxide is comparatively stable in the gas phase. This is suggested also by its behaviour in the present system, when it survived in a heated vessel after it had been generated by the reaction of COS with oxygen atoms.

The reaction between COS and O atoms is believed to yield only ground state products when neither reactant is in an excited state (191), and is then 52 kcal/mole exothermic (its activation energy is of about 6 kcal/mole (192)). Observation by ESR revealed no excited SO to be formed when the O atoms were produced by the NO + N reaction (191), and the production of electronically excited CO would make the reaction endothermic. Of possible side reactions, the reaction

$$COS + O_2 \longrightarrow SO + CO_2$$

should be of little significance in the present system, with its negligible O_2 concentration; both the short reaction distance between the point of O atom formation and the COS inlet jet, and the elevated reaction temperature preclude an appreciable concentration of oxygen molecules. Similarly, the reaction

$$COS + O \longrightarrow CO_2 + S$$

apparently did not occur, since no sulphur was ever deposited in any part of the system in the absence of active nitrogen. Moreover, a mass spectrometric study on the COS-O system has indicated that CO and SO were 1000 times as abundant as CO_2 and S (193).

The reaction of SO with atomic nitrogen yielded sulphur in a narrow band close to the SO inlet jet. This clearly indicated a fast reaction between SO and nitrogen atoms to form NO and S. Apparently, the S atoms were not removed rapidly enough by atomic nitrogen to prevent deposition of sulphur on the wall. This agrees with the conclusions of a previous study (133).

It is interesting to consider the reactions that might have tended to decrease the yield of SO from the oxidation of COS. Loss of SO by its reaction with O atoms to form SO_2 was probably negligible; such a reaction would likely be third order. Disproportionation of SO to form SO_2 + S also seems to have been insignificant (see later) in disagreement with the relatively large rate constant estimated previously for this reaction (138). Had disproportionation been serious, it is quite improbable that the rate constant for the N + SO reaction should have remained unaltered as it did (Table XXIX), for different distances between the SO generator and the point at which SO was introduced into the active nitrogen. Moreover, if disproportionation had been significant in the present system, sulphur should have formed throughout the main reaction vessel, in the absence of atomic nitrogen, whereas no trace of sulphur was ever detected under such conditions.

The apparent discrepancy between the present and the earlier study in respect of the disproportionation of SO, might result from the use of a large excess of COS in the previous investigation, that might have permitted removal of SO by several possible exothermic processes. (It is interesting that the analogous process, $SO + O_2 \rightarrow SO_2 + O$, which is about twice as exothermic as $SO + SO \longrightarrow SO_2 + S$, has a relatively low rate constant.)

If other reactions had consumed SO before the SO-active nitrogen reaction could occur, the disappearance of SO would then have satisfied a relation of the type,

$$-d[SO]/dt=k_1[SO][O][M]+k_2[SO]^2+k_3[SO]+\text{other terms including active nitrogen}$$

where k_1, k_2, k_3, are respectively, the rate constants associated with SO combination with oxygen atoms, SO disproportionation, and removal of SO catalytically at the wall. The plot of $\frac{1}{t}(\ln[N]_o/[N]_t)$ against $2[SO]_t$ (Fig. 20) should then not have been linear, or it should have shown an intercept on the ordinate.

The essentially quantitative yield of SO from the COS + O reaction was readily checked. It has been established (194) that both oxygen atoms and SO undergo fast reactions with NO_2; the NO_2-SO reaction is even faster than the NO_2-O reaction. Carbonyl sulphide was therefore added to oxygen atoms produced by the NO + N reaction until the $SO_2{}^*$ emission in the N_2 carrier gas was almost extinguished, and then NO_2 was added downstream to titrate the products. The reactions pertinent to the experiment were assumed to be

$$COS + O \longrightarrow CO + SO \quad ..... \ (1)$$

$$SO + O \longrightarrow SO_2 + h\nu \quad ..... \ (2)$$

$$SO + NO_2 \longrightarrow SO_2 + NO \quad ..... \ (3)$$

As long as the flow rate of NO_2 was below that of SO, reaction (2) produced the purple light emission. The flow rate of NO_2 that gave complete extinction of reaction (2) was then compared with the NO_2 flow rate that corresponded to the complete consumption of oxygen atoms in the absence of COS. Since the two titration values agreed within 5%, it would appear that the COS + O reaction did yield SO quantitatively.

The blue emission observed during the COS + O reaction is probably the result of the reaction

$$SO + O \longrightarrow SO_2{}^* \longrightarrow SO_2 + h\nu$$

The other possible emission process,

$$CO + O \longrightarrow CO_2{}^* \longrightarrow CO_2 + h\nu$$

has a higher energy barrier for light emission (195); moreover, the CO + O reaction is probably third order at 2 torr pressure, with an activation energy of 3.5 kcal/mole. These conclusions are supported by a spectroscopic study (196) in which it was found that the spectrum for the $SO_2{}^*$ emission, resulting from a discharge through an SO_2/Ar mixture, was similar to the spectra obtained by the oxidation of COS, H_2S and CS_2 by atomic oxygen.

When the O atom, or COS flow rate in the auxilliary vessel was less than the N atom flow rate in the main reactor, the yellow afterglow was only partially quenched. Simultaneous estimation of the residual N atom flow rate showed that consumption of active nitrogen was equal to twice the flow rate of O atoms or COS. On the other hand, the O atom, or COS flow rate could be adjusted to quench the afterglow completely in the main reactor, and the flow rate necessary to do so was one-half the flow rate of N atoms in that vessel. The afterglow could be made to reappear by merely reducing the O atom, or COS flow rate below that corresponding to darkness in the reaction tube.

The differential rate equation appropriate to the reaction is $-d[N]/dt = 2k[SO][N]$. On integration this yields

$$kt = \frac{\ln([N]_o/[N]_t)}{2[SO]_o - [N]_o + [N]_t}$$

The rate constants are summarized in Table XXIX.

TABLE XXIX

Rate Constants for the Reaction of Sulphur Monoxide with Atomic Nitrogen

Reaction temperature 300°K
(Values based on data in Table XX)

k
(cc/molec-sec)x10^{12}

Total pressure 2 torr SO generator at 225°C	Total pressure 2.5 torr SO generator at 400°C	Total pressure 3.5 torr SO flow line to reactor altered
1.7	2.2	1.5
1.5	1.3	1.5
1.5	1.6	1.5
1.5	1.5	1.6
1.5	1.5	1.6
1.5	1.4	1.5

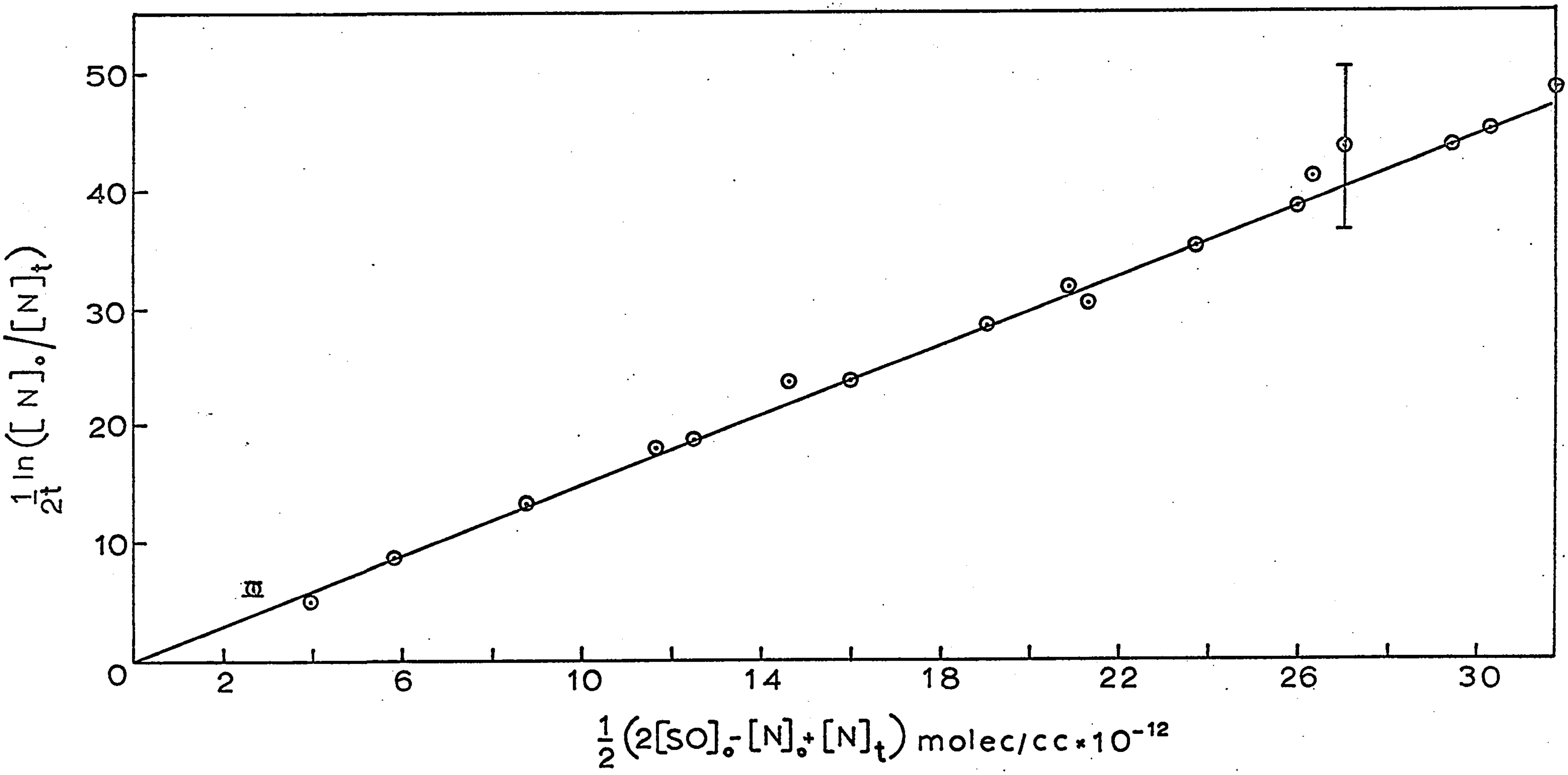
It should be noted that whereas the data in the left-hand side column of Table XXIX were obtained with the SO generator heated to about 225°C, the generator was heated

Figure 20

Reaction of Sulphur Monoxide with Atomic Nitrogen at 300°K

$$\frac{1}{2t}\ln([N]_o/[N]_t) \quad \underline{\text{vs.}} \quad \frac{1}{2}(2[SO]_o-[N]_o+[N]_t)$$

(Results from Table XX)



$\frac{1}{2t}\ln([N]_o/[N]_t)$
0
10
20
30
40
50
2
6
10
14
18
22
26
30
$\frac{1}{2}(2[SO]_o-[N]_o+[N]_t)$ molec/cc×10^{-12}

to 400°C for the data in the middle column. This was done to ascertain whether secondary reactions within the generator might interfere seriously with the behaviour of the system. It would appear that such reactions were not important. The change in total pressure from 2 to 2.5 torr was without effect on the rate constant.

Further increase of the total pressure to 3.5 torr also left the rate constants unaltered (right-hand side column Table XXIX), which, moreover, were attained after the flow line between the SO generator and the main reaction vessel had been first decreased and then increased in length by a factor of 3. This was done to reveal any effect of disproportionation of SO that might occur after it left the heated generator, and it seems clear, from the data, that such effects were not significant.

The data in Table XX are plotted in Fig. 20. From the slope of the line an average rate constant of $(1.5\pm0.2)\mathrm{x}10^{12}$ cc/molec-sec may be calculated for the reaction of SO with active nitrogen.

The uniform rate constants from this study indicate the efficiency of nitric oxide in terminating the reaction in the gas phase by the rapid removal of nitrogen atoms.

The insignificant pressure dependence of the reaction rate constant (in the region 2 to 3.5 torr) indicates that the reaction of SO with atomic nitrogen does not involve a third body in its rate determining step. However, it cannot exclude subsequent pressure dependent processes.

The constancy of the rate coefficients may also suggest that mixing effects, in the relatively short reaction times used, were practically insignificant. (This may in turn indicate a fast reaction between SO and N.)

No attempt was made to determine an activation energy for the reaction, owing to its high rate even at 300°K. It is likely, however, that this reaction, like the NO reaction ($k \approx 10^{-11}$ cc/molec-sec), has practically zero activation energy. (In fact, it represents the exchange reaction between two radicals that generally proceeds with zero activation energy.) The relatively large value of its rate constant (only about 2 orders smaller than the bimolecular collision number) is in agreement with the relatively large steric factors observed for abstraction reactions.

VI. THE REACTIONS OF SULPHUR TRIOXIDE WITH OXYGEN AND NITROGEN ATOMS

There was some temporary lack of stability in the SO_3 reaction system after it had been cleaned. It has been noted previously (197) that the presence of SO_3 increases recombination of oxygen atoms at a wall. In the present system, this effect seemed to be time dependent, and reasonably reproducible results were obtained only after the reaction vessel had been flushed a number of times with SO_3 in the absence of atomic oxygen or atomic nitrogen. It might well be that part, at least, of the difficulty was due to attack of SO_3 on the stopcock grease, and that this contributed to irreproducibility until, perhaps, more easily attacked components in the grease responded less readily to the presence of SO_3.

The negligible amounts of SO_3 found during the reaction of SO_2 with active nitrogen from a condensed discharge might be expected if it is formed in a third order reaction, and if its consumption by the active species is also relatively slow. Atomic nitrogen, atomic oxygen and possibly electronically excited nitrogen molecules are the only reactive species that could cause decomposition of SO_3 in this system. It is not likely that ozone contributed significantly as a reactant with SO_3, since no ozone was found in the cold trap when O atoms were produced by the NO titration of nitrogen atoms from a microwave discharge in the absence of SO_3. Besides, other studies (198) have shown that ozone formation is a three body process, $O + O_2 + M \longrightarrow O_3 + M$, that seems to occur mainly on a cold surface, and none was found in a stream of oxygen that has been subjected to an electrical discharge.

The reaction of SO_3 with O atoms and also that with N atoms, yielded SO_2 as a stable product. Its apparent constant rate of formation, for a particular reaction time, and the satisfactory rate constants obtained (Tables XXX, XXXII showed that the low temperature trapping method was adequate for stopping these reactions, as it had been demonstrated to be for the reaction of active nitrogen with ethylene (199)).

The reaction of SO_3 with atomic oxygen appears to be a relatively slow, simple bimolecular reaction, the rate constants for which were calculable from simple second order kinetics. The slowness of the reaction is probably associated with a low steric factor in the rate controlling step, since its activation energy is low in the temperature range $300^{o}K-500^{o}K$.

A metastable solid product, of relatively low melting point (0-20°C), was probably sulphur tetra-oxide, SO_4. This entity may be prepared (200,201) by a glow or silent discharge through a mixture of SO_2 or SO_3 with excess O_2. The gas phase formation of a similar complex by an addition reaction

$$SO_3 + O \longrightarrow SO_4^*$$

might be associated with a low probability term, corresponding to the formation of a new S-O bond. A possible back reaction

$$SO_4^* \longrightarrow SO_3 + O$$

might be in competition with the decomposition to stable products, $SO_4^* \longrightarrow SO_2 + O_2$. However, in this event a temperature increase should have affected the rate of the reaction, since high temperature should not favour the formation of the addition complex (which would presumably be promoted by a low temperature "sticky" collision process), and fewer SO_4^* molecules should be formed. This, however, was not observed in at least the majority of the experiments. In fact, formation of SO_2, for a particular reaction time, was constant over a temperature range from 300^{o} to $500^{o}K$

(Table XXIV). This suggests that any reduction in the amount of $SO_4{}^*$ present, with increase of temperature, was compensated by an increased dissociation of the complex to $SO_2 + O_2$.

The reactions that lead to SO_2 formation might then be

$$SO_3 + O \longrightarrow SO_4{}^* \longrightarrow SO_2 + O_2 \qquad .....(14)$$

$$SO_3 + O \longrightarrow SO_4{}^{**} \xrightarrow{\Delta} SO_2 + O_2 \qquad .....(14a)$$

where the latter, as a wall reaction in the cold trap may be considered to produce an addition complex that yields a fraction of the total SO_2 production as the ambient temperature is raised.[ϕ]

The rate data recorded for the reaction of SO_3 with O may then be taken to correspond to formation of $SO_4{}^*$, which subsequently dissociates spontaneously to stable products. The rate constant was obtained by integrating the expression for SO_3 removal by O atoms,

$$k_{14}t = \frac{\ln\left([SO_3]_o / ([SO_3]_o - [SO_2]_t)\right)}{[O]_o - [SO_2]_t}$$

where

$[SO_3]_o, [O]_o$ = initial SO_3 and O atom concentrations, respectively

$[SO_2]_t$ = SO_2 concentration present at time t

t = reaction time

[ϕ] The relatively smaller contribution of reaction (14a) to SO_2 production as observed in this study, may be interpreted to indicate that under these conditions recombination of oxygen atoms had been the predominating process.

The data of Table XXX and Fig. 21 gave an average rate constant of $(5.6 \pm 0.6) \times 10^{-17}$ cc/molec-sec. which was practically temperature independent in the range 300 to 500°K (same Table).

TABLE XXX

Rate Constants for the Reaction of Sulphur Trioxide with Oxygen Atoms

Total pressure 2 torr
(Values based on data in Table XXIV)

	SO_3 input (mole/sec)x10^6	k_{14} (cc/molec-sec)x10^{17}
300°K:	4.65	5.3
	6.00	5.8
	8.20	6.0
	9.80	5.5
	12.50	6.5
	14.40	6.3
	19.0	5.6
	20.6	4.5
413°K:	6.00	5.8
	9.80	5.5
	14.60	6.4
	17.10	5.0
	20.3	4.5
500°K:	4.65	5.3
	7.20	5.5
	7.90	7.2
	9.30	6.0
	12.50	6.4
	19.0	5.6

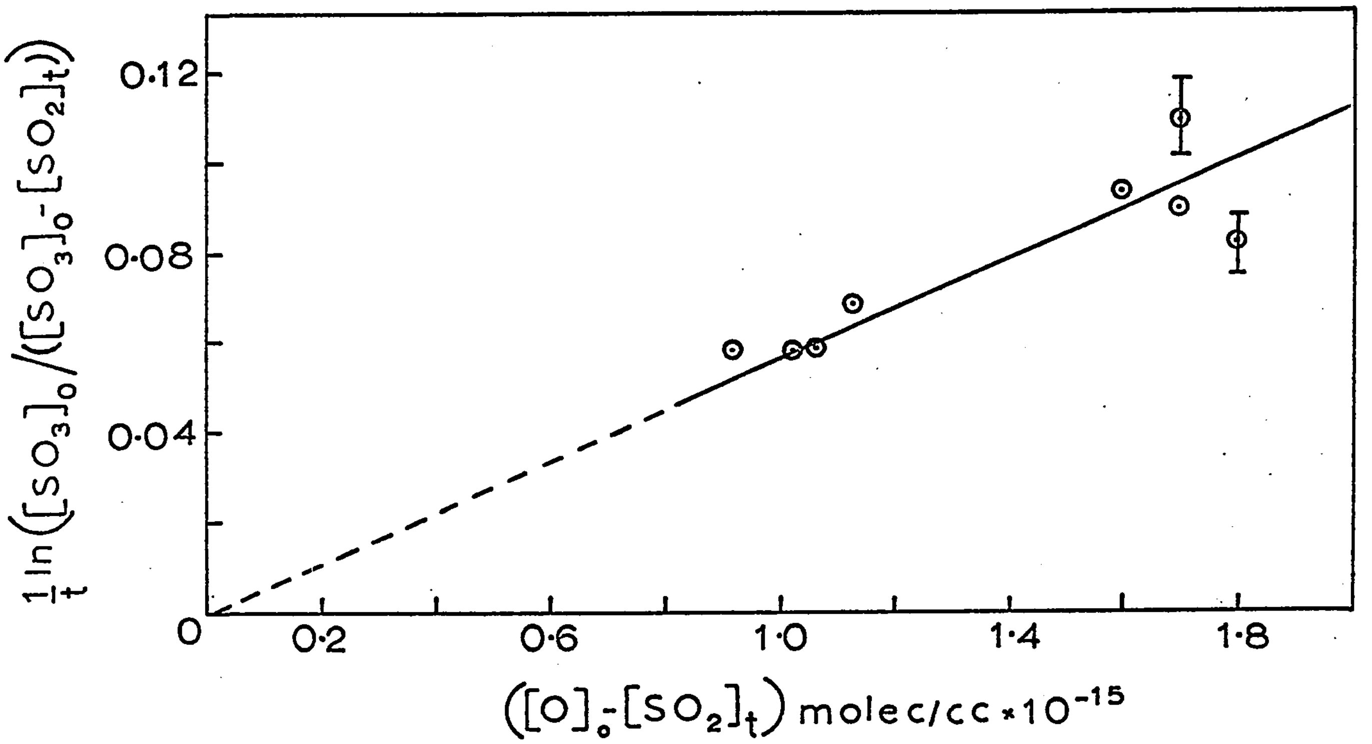
The only other rate data reported for this reaction are those obtained during a high temperature flame study (202), in which an average rate constant was estimated for the overall

Figure 21

Reaction of Sulphur Trioxide with
Oxygen atoms at 300°K

(Reaction terminated by low temperature trapping)

Plot of $\frac{1}{t} \ln ([SO_3]_o/([SO_3]_o-[SO_2]_t)$ vs. $([O]_o-[SO_2]_t)$


$\frac{1}{t}\ln\left([SO_3]_0/([SO_3]_0-[SO_2]_t)\right)$
0·12
0·08
0·04
0
0·2
0·6
1·0
1·4
1·8
$([O]_0-[SO_2]_t)$ molec/cc × 10^{-15}

destruction of SO_3 by both atomic oxygen and atomic hydrogen. The reported value is 1.5×10^{-12} cc/molec-sec at $1600^{o}K$, but it is not possible to resolve this value into the separate constants for each of the atom reactions involved.

The reaction of SO_3 with atomic nitrogen also obeyed second order kinetics and yielded uniform rate constants. It is worth noting, perhaps, that the information contained in Table XXIa was not used for estimating the rate constants when the reaction was terminated with nitric oxide. The values reported in this table indicated that the flow rate of atomic nitrogen remained unaltered along the reaction tube in the absence of SO_3. This suggests that the wall was "poisoned" against heterogeneous N atom recombination, presumably because the NO titrations were made at the upper end of the reaction vessel before subsequent experiments were made downstream, and the oxygen atoms caused partial wall "poisoning" below the titration level. On the other hand, the data in Table XXIb do not show this effect, since the NO titrations were begun at the lower end of the reaction tube. These results are probably more trustworthy, and may be assumed to correspond to a simple sequence

$$SO_3 + N \longrightarrow (SO_3.N) \longrightarrow SO_2 + NO \qquad .....(15)$$

$$NO + N \longrightarrow N_2 + O \qquad ..... (5)$$

At the temperatures used, there was apparently no significant contribution from the slower, probably consecutive reaction

$$SO_3 + O \longrightarrow SO_4^* \longrightarrow SO_2 + O_2 \qquad .....(14)$$

The rate constant was calculated from

$$k_{15}t = \frac{2 \ln ([SO_3]_o/([SO_3]_o - [N]_o/2 + [N]_t/2)}{[N]_o + [N]_t}$$

where $[N]_o$, $[N]_t$ = initial and final N atom concentration, respectively, and the other quantities have their former significance. This expression was obtained by integration of the differential rate expression, $-d[SO_3]/dt = k_{15}[SO_3][N]$, where instantaneous concentrations of SO_3 were expressed in terms of initial and final N atom concentrations.

The data of Table XXXI and Fig. 22 gave an average rate constant of $(4.5 \pm 0.7) \times 10^{-16}$ cc/molec-sec. This value may be compared with that obtained when the reaction was terminated by the low temperature trapping procedure. This method permitted the course of the reaction to be followed by estimating the formation of SO_2 as a function of reaction time. The corresponding rate constant was calculated from the expression

$$k_{15}t = \frac{\ln ([SO_3]_o/([SO_3]_o - [SO_2]_t))}{[N]_o - [SO_2]_t}$$

where $[SO_2]_t$ = SO_2 concentration present at time t, and other symbols have their earlier connotation. The data are shown in Table XXXII and Fig. 23 from which an average rate constant of $(5.4 \pm 0.5) \times 10^{-16}$ cc/molec-sec may be evaluated.

It is evident that agreement was good between rate constants obtained by terminating the reaction with NO and by terminating it with the low temperature trapping technique.

TABLE XXXI

Rate Constants for the Reaction of Sulphur Trioxide with Atomic Nitrogen

(Reaction terminated by nitric oxide)
Temperature 300°K
(Values based on data in Table XXIb)

NO flow (mole/sec)x10^6	k_{15} (cc/molec-sec)x10^{16}
1.26	4.3
1.40	4.4
1.56	4.7
1.70	4.6

The values were some 10 times larger than those for the SO_3 + O reaction.

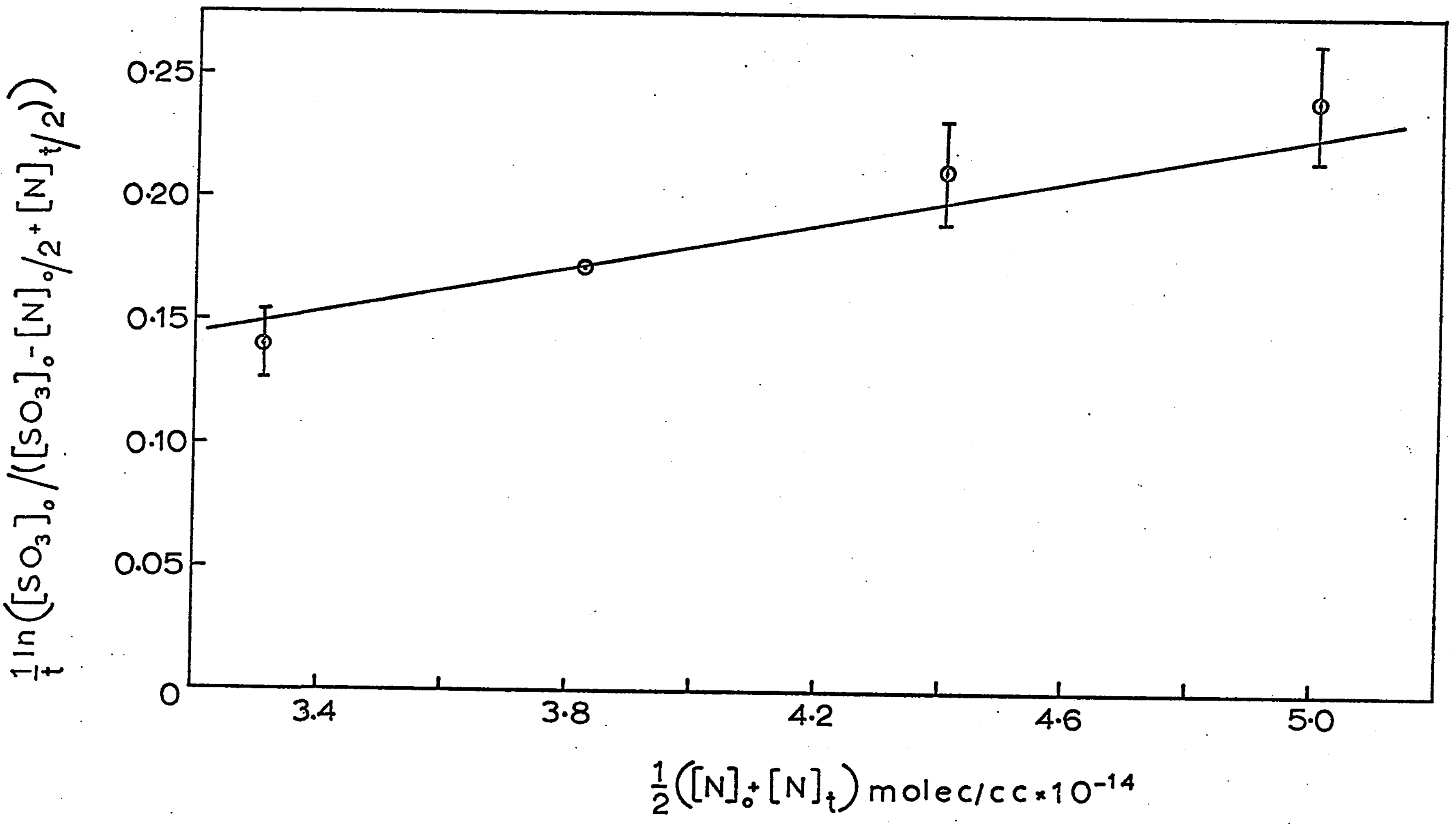
Data for temperatures of 413°K and 523°K, with somewhat higher total pressures than that at 300°K, are shown in Table XXXII and Fig. 24. The results give, respectively, average rate constants of $(1.3 \pm 0.1) \times 10^{-15}$ and $(2.8 \pm 0.3) \times 10^{-15}$ cc/molec-sec. A relatively low activation energy of about 2.3 kcal/mole (Fig. 25) was evaluated from the data for the range of temperatures between 300 and 523°K.

It is rather difficult to assess the configuration of the initial $(SO_3.N)$ complex, which need not be identical with the configuration of the intermediate from which the stable products emerge. (The assignment of structural parameters to such a complex may be based on some "educated guesses", the validity of which becomes increasingly questionable as the number of atoms in the complex is increased.) However,

Figure 22

Reaction of Sulphur Trioxide with Atomic Nitrogen
(Reaction terminated by NO)

Plot of $\frac{1}{t}\ln([SO_3]_o/([SO_3]_o-[N]_o/2+[N]_t/2))$ vs. $\frac{1}{2}([N]_o+[N]_t)$



0·25
0·20
0·15
0·10
0·05
0
3.4
3·8
4·2
4·6
5·0
$\frac{1}{t}\ln([SO_3]_o/([SO_3]_o-[N]_o/2+[N]_t/2))$
$\frac{1}{2}([N]_o+[N]_t)$ molec/cc×10^{-14}

TABLE XXXII

Rate Constants for the Reaction of Sulphur Trioxide with Atomic Nitrogen

Reaction terminated by low temperature trapping
(Values based on data in Tables XXII, XXIII)

Temperature 300°K		Temperature 413°K		Temperature 523°K	
SO_3 input mole/sec)x10^6	k_{15} (cc/molec-sec)x10^{16}	SO_3 input (mole/sec)x10^6	k_{15} (cc-molec-sec)x10^{15}	SO_3 input (mole/sec)x10^6	k_{15} (cc/molec-sec)x10^1
5.20	4.8	8.00	1.3	6.56	2.8
5.20	5.5	12.50	1.2	6.56	2.8
7.00	4.4	15.50	1.3	6.56	2.7
7.00	5.8	15.50	1.3	6.56	2.9
9.90	5.1	-	-	12.50	2.3
9.90	5.1	-	-	15.50	2.7
12.80	5.5	-	-	-	-
13.30	5.4	-	-	-	-
13.30	5.4	-	-	-	-
17.00	5.2	-	-	-	-

Figure 23

Reaction of Sulphur Trioxide with Atomic Nitrogen at 300°K

(Reaction terminated by low temperature trapping)

Plot of $d[SO_2]/dt$ vs. $([SO_3]_o-[SO_2]_t)([N]_o-[SO_2]_t)$

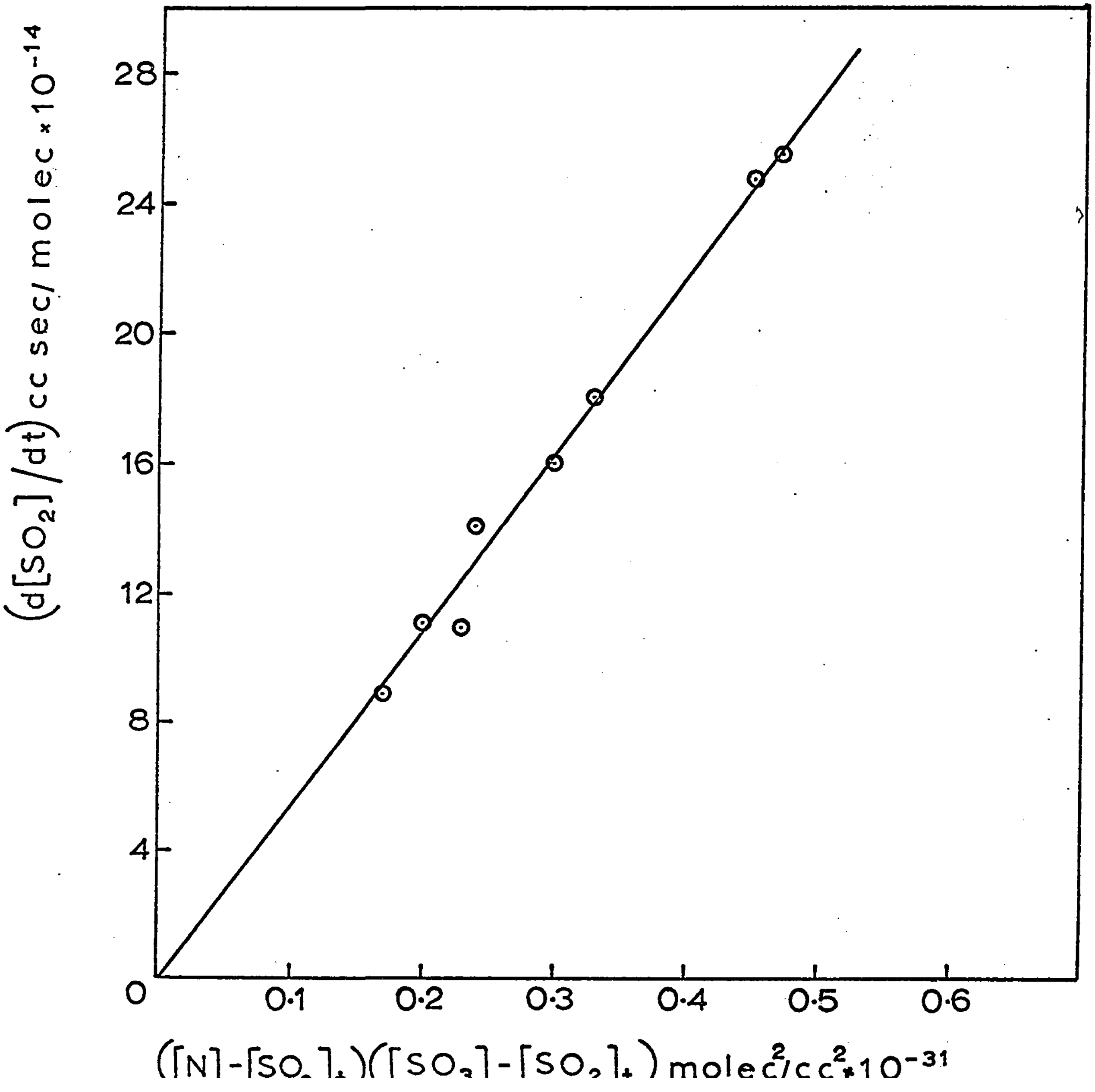

$(d[SO_2]/dt)$ cc sec/ molec × 10^{-14}
0
4
8
12
16
20
24
28
0·1
0·2
0·3
0·4
0·5
0·6
$([N]-[SO]_t)([SO_3]-[SO_2]_t)$ molec^2/cc^2 × 10^{-31}

Figure 24

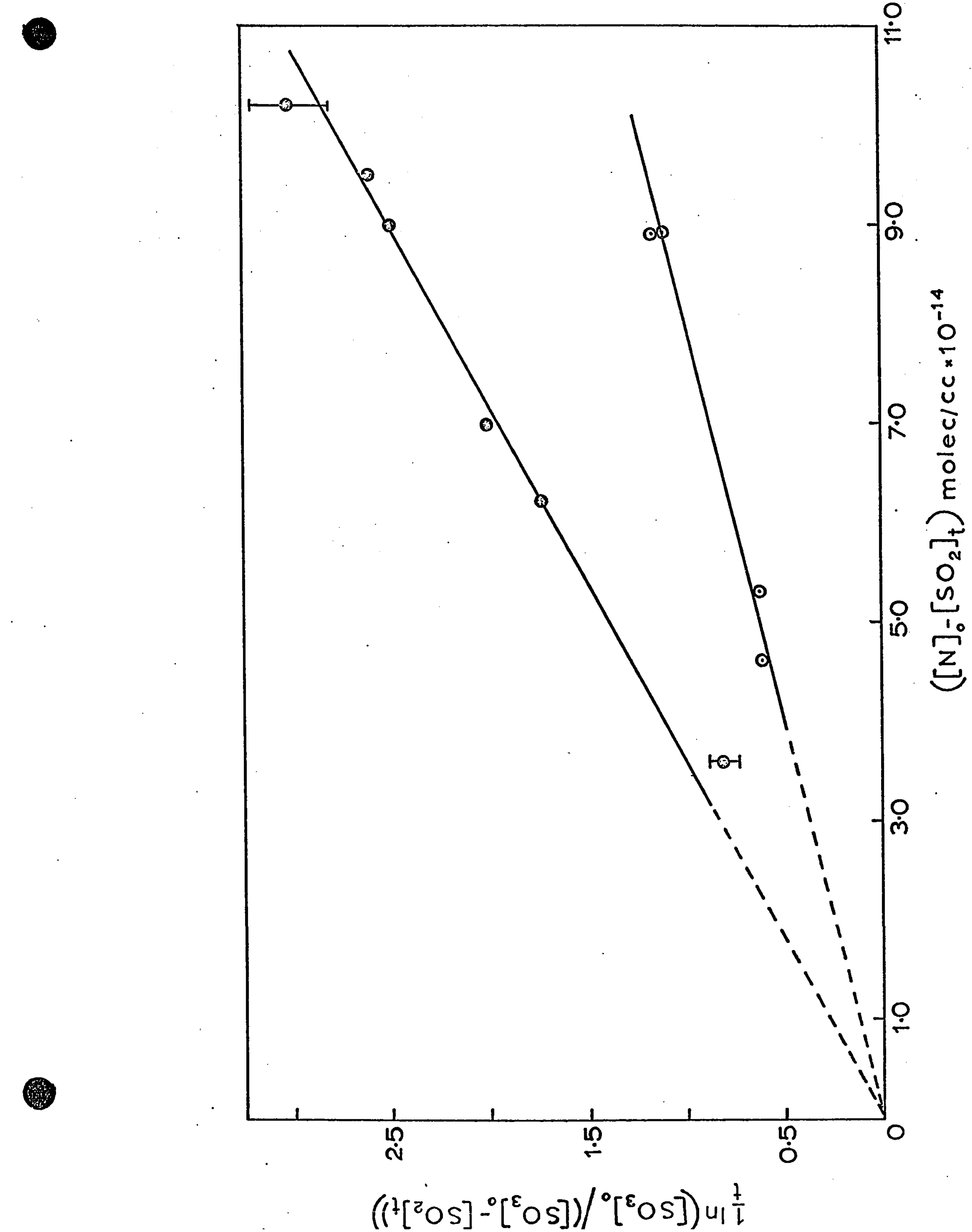
Reaction of Sulphur Trioxide with Atomic Nitrogen at Elevated Temperatures

(Reaction terminated by low temperature trapping)

Plot of $\frac{1}{t}\ln([SO_3]_o/([SO_3]_o-[SO_2]_t))$ vs. $([N]_o-[SO_2]_t)$

○ - at 413°K

● - at 523°K


2.5
1.5
0.5
0
1.0
3.0
5.0
7.0
9.0
11.0
$\frac{1}{t}\ln([SO_3]_0/([SO_3]_0-[SO_2]_t))$
$([N]_0-[SO_2]_t)$ molec/cc ×10^{-14}

it seems plausible to assume that nitrogen atoms interact with the semi-double bonding system in SO_3, to form a transition state within which rearrangement may occur to form a transient species (not isolated) that subsequently dissociates into stable products. The formation of this complex is probably rate determining, with a relatively low frequency factor (1.7×10^{-14} cc/molec-sec, Arrhenius plot Fig. 25).

Instead of assuming, as in the calculations of k_{15}, that the reaction of O atoms with SO_3 makes negligible contribution to the consumption of SO_3, it is possible to treat the total consumption of SO_3, as the result of a competitive, consecutive second order process - reactions (15), (5) and (14). Since reaction (15) is followed by the very fast reaction (5), the sequence may then be treated kinetically (203) to yield the ratio $K = k_{14}/k_{15}$ as an implicit function of any two simultaneous concentrations present at a single time.

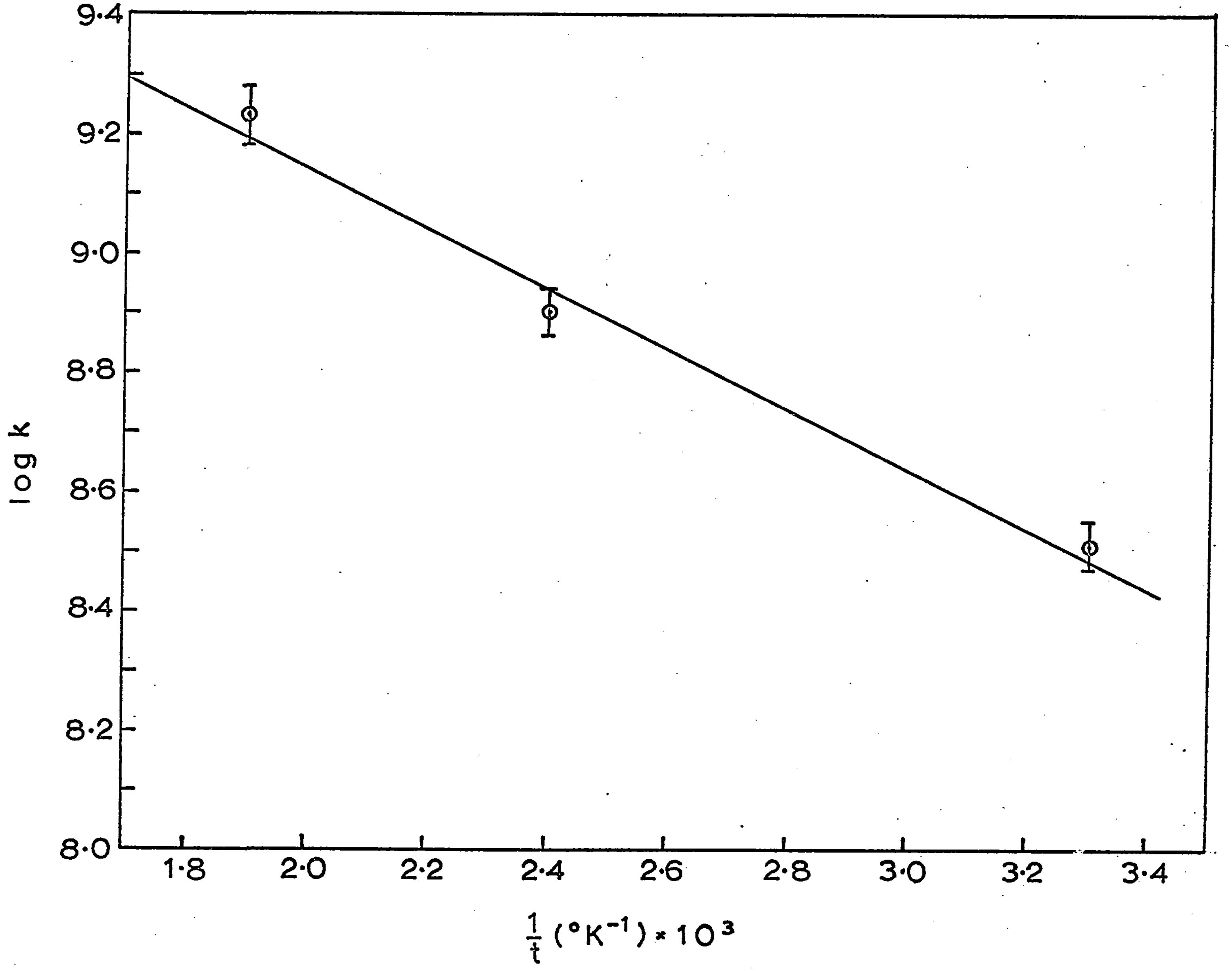
TABLE XXXIII

Reaction of Sulphur Trioxide with Atomic Nitrogen
Temperature Dependence

k_{15} (cc/mole-sec)$\times 10^{-8}$	T (^{o}K)
3.2	300
7.8	413
16.9	523

Figure 25

Arrhenius Plot for the Reaction of Sulphur Trioxide with Atomic Nitrogen


9·4
9·2
9·0
8·8
8·6
8·4
8·2
8·0
log k
1·8
2·0
2·2
2·4
2·6
2·8
3·0
3·2
3·4
$\frac{1}{t}$ (°K^{-1}) × 10^3

The rates of change of $[N]$ and $[O]$ with time are:

$$-d[N]/dt = k_{15}[SO_3][N] \qquad \ldots\ldots (1)$$

$$-d[O]/dt = k_{15}[SO_3][N] - k_{14}[SO_3][O] \qquad \ldots\ldots (2)$$

If $K = k_{14}/k_{15}$, $\beta = [N]_t/[N]_o$ and $\gamma = [O]_t/[N]_o$, and equation (2) is devided by equation (1) in terms of the new variables,

$$d\gamma/d\beta = K\frac{\gamma}{\beta} - 1$$

This may be integrated for the variables, β and $\gamma = \beta y$ with the boundary conditions, initial (1,0) final (β,γ), to give

$$\beta^K = \beta + \gamma(1-K)$$

The value of K that satisfies this relation may be found for any measured pair (β,γ) of the experimental concentrations. With an IBM 7040 digital computer, several values of β and γ were used to calculate values of K and k_{15}, at 300, 433 and 523°K, with the following results:

TABLE XXXIV

Reaction of Sulphur Trioxide with Atomic Nitrogen
Data for Estimation of k_{15}

	$\beta = [N]_t/[N]_o$	$\gamma = [O]_t/[N]_o$	K	k_{15} (cc/molec-sec)
300°K:	0.70	0.295	0.088	6.3×10^{-16}
	0.73	0.266	0.088	6.3
	0.61	0.381	0.085	6.6
	0.72	0.271	0.088	6.3
	0.65	0.341	0.088	6.3
	0.83	0.166	0.088	6.3
	0.57	0.417	0.085	6.6
433°K:	0.61	0.385	0.048	1.2×10^{-15}
	0.53	0.459	0.049	1.1
	0.63	0.363	0.048	1.2
	0.60	0.393	0.046	1.2
	0.49	0.499	0.048	1.2
523°K:	0.62	0.378	0.0200	2.8×10^{-15}
	0.65	0.344	0.0221	2.5
	0.58	0.416	0.0202	2.8
	0.67	0.325	0.0181	3.1
	0.48	0.512	0.0210	2.7

With the experimental value from the present study for k_{14} of $(5.6 \pm 0.6) \times 10^{-17}$ cc/molec-sec, and K values of 0.088, 0.048, 0.0200, the calculated values of k_{15} are $(6.3 \pm 0.6) \times 10^{-16}$, $(1.2 \pm 0.1) \times 10^{-15}$, and $(2.8 \pm 0.3) \times 10^{-15}$ cc/molec-sec at temperatures of 300, 433 and 523°K, respectively. These are in excellent agreement with the experimental values of k_{15} at these temperatures reported in Table XXXII.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. A condensed discharge was found to exhibit a long delay, and a microwave discharge only a short delay, in reverting from a "poisoned" to an "unpoisoned" condition when the impurity gas (H_2 or H_2O) was removed. A reduction in the voltage necessary to sustain the discharge as well as comparable enhancement of the active nitrogen concentration was found with H_2 and H_2O. However, the effect of these gases on the N atom yield was much smaller with a microwave than with a condensed discharge.

While adsorption of the impurity gas in the discharge tube might explain some of the effects observed, it seems likely that the impurity is directly involved in the dissociation process to increase the yield of atoms, and that fewer electronically excited molecular species, N_2^*, are formed in the microwave than in the condensed discharge.

2. No decomposition of NH_3 and SO_2 was observed in an "unpoisoned" microwave or condensed discharge system. However, distinct decomposition of NH_3 and SO_2 was observed in a "poisoned" condensed discharge, but practically none in a "poisoned" microwave discharge of comparable N atom concentration. It is unlikely that the "poison" present was responsible for initiating the observed destruction of SO_2, because of the inherent endothermicity of any reactions that might reasonably be involved.

3. Practically constant SO_2 destruction was observed for different N atom concentrations, and a slight but perceptible partial quenching of the yellow afterglow in the presence of SO_2 occurred. The behaviour suggested that SO_2 is decomposed by energy transfer from excited nitrogen molecules, probably $N_2(A^3\Sigma_u^+)$, the concentration of which is little affected by the presence of N atoms, and from which lower levels of the $N_2(B^3\Pi_g)$ state might be populated.

4. The stable products of the decomposition of SO_2 by active nitrogen are SO_3, presumably as a result of the reaction $SO_2 + O + M$, and sulphur nitrides (S_4N_4, S_2N_2, $(SN)_x$) that probably result from a third order reaction of N atoms with S atoms. The O and S atoms are probably derived from SO which is presumably formed as a transient in the system, and is a precursor to the sequence

$$SO + N \longrightarrow NO + S$$

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

5. The NO titration value (N atom flow rate) decreased to a plateau value with increase of either NH_3 and SO_2 flow rate. Evidently, NO deactivates the species responsible for NH_3 or SO_2 destruction. The relative behaviour of the NO titration in the presence of these gases suggests that NH_3 is more efficient than SO_2 for deactivating $N_2(A^3\Sigma_u^+)$.

6. Production of HCN from CH_4, C_2H_6 and cyclopropane is suppressed in the presence of NH_3 and SO_2. Hence the reactive

species removed by these two gases probably initiates the reactions with the hydrocarbons that ultimately lead to HCN production. At room temperature, production of HCN from CH_4 and C_2H_6 was suppressed to an increasing extent as the flow rate of NH_3 or SO_2 was increased. Hence, the decomposition products of NH_3 and SO_2 (e.g., H atoms and O atoms, respectively) probably did little to facilitate HCN production under these conditions. On the other hand, SO_2 was more effective than NH_3 in suppressing the HCN yield from cyclopropane, which implies that H atoms from the decomposition products of NH_3 attack this hydrocarbon more readily than do O atoms.

7. A slight decrease in the HCN production from ethylene was observed in the presence of low NH_3 flow rates, but not with low SO_2 flow rates. This suggests either that some N atoms react with the decomposition products of NH_3, or possibly, that HCN production from C_2H_4 is initiated by attack of C_2H_4 by excited nitrogen molecules. As the flow rate of NH_3 or SO_2 was increased, the HCN yield from C_2H_4 approached a plateau value. With NH_3, this level was comparable with that of the NO titration value. Presumably, H or O atoms lead to formation of radicals (e.g., C_2H_5 or CHO) which react readily with N atoms. This suggests that the maximum HCN yield from ethylene alone is not a true measure of the nitrogen atom content. The HCN plateau value attained in the presence of SO_2 was lower than the NO titration value, probably because N atoms were consumed in this system by the intermediates SO and NO.

8. The yields of HCN from propane and n-butane, in the presence of NH_3, were promoted to a larger extent than in the presence of SO_2 (at high hydrocarbon flow rate). This might be explained if propyl and butyl radicals, formed in the presence of H atoms from NH_3, were more readily attacked by N atoms to form HCN than the products (perhaps carbonyl compounds) of O atom attack on these hydrocarbons.

9. The CN chemiluminescence during a hydrocarbon-active nitrogen reaction was quenched by addition of rather specific amounts of NH_3 and SO_2, but formation of HCN was never completely suppressed. Instead, it tended to become constant at high hydrocarbon flow rates. This suggested a residual reaction of the hydrocarbon with a species not consumed by NH_3 or SO_2, presumably nitrogen atoms. (There would seem to be also little relation between the intensity of the emission of the CN bands and the formation of HCN).

10. The limiting extent of SO_2 decomposition by active nitrogen passed through a flat maximum with increase of SO_2 flow rate. The decomposition was pressure independent in the range 2 to 3 torr, which suggested that SO_2 itself might be responsible for the effect.

11. Second order overall rate constants were calculated for the decomposition of SO_2 by active nitrogen, on the seemingly justifiable assumption that the reaction $N_2^* + SO_2 \longrightarrow SO_2^* + N_2$ is the rate controlling step. The excited

SO_2 molecule formed, $SO_2{}^*$, is assumed to disappear relatively fast by subsequent spontaneous decomposition, or by the attack of N atoms. The results yielded consistently lower rate constants for higher initial flow rates of SO_2. This was attributed to the self-deactivation process $SO_2^* + SO_2 \rightarrow SO_2 + SO_2$.

12. The rate constant for the energy transfer,

$$N_2^* + SO_2 \rightarrow SO_2^* + N_2$$

was estimated to be $7\text{x}10^{-15}$ cc/molec-sec, and the overall decomposition by active nitrogen is associated with an activation energy of about 2 kcal/mole and a steric factor of approximately $2\text{x}10^{-4}$. The relatively low temperature dependence is typical of energy transfer processes, while the relatively low steric factor may suggest a spin disallowed energy exchange. Non-conservation of spin in this case might be compensated by the relatively long life-time of the energy donor, the $N_2(A^3\Sigma_u^+)$ molecule.

13. The ratio k_4/k_3 associated with the parallel reactions

$$SO_2^* + N \rightarrow SO + NO \qquad \ldots\ldots(3)$$

$$SO_2^* + SO_2 \rightarrow SO_2 + SO_2 \qquad \ldots\ldots(4)$$

was found to be about 10.

14. The reaction of SO with nitrogen atoms was fast and yielded elemental sulphur near the SO inlet jet. No sulphur was formed in the absence of atomic nitrogen, which suggested a negligible disproportionation of SO to SO_2 and S in this system.

15. The yield of SO in a heated (225°C) generator from the reaction of COS and O atoms was shown to be quantitative by the NO_2 titration of SO and oxygen atoms. This reflects a relatively negligible extent of the possible reactions

$$SO + O \longrightarrow SO_2^* \longrightarrow SO_2 + h\nu$$

and

$$CO + O \longrightarrow CO_2^* \longrightarrow CO_2 + h\nu$$

in the heated generator.

16. Kinetic measurements on the reaction of SO with N atoms gave a rate constant of $(1.5 \pm 0.2) \times 10^{-12}$ cc/molec-sec at 300°K, which was independent of pressure in the range 2 to 3.5 torr.

17. The reaction of SO_3 with O atoms was found to be slow and its rate to be practically independent of temperature in the range 300 to 500°K. This suggests a low steric factor for the reaction. A melastable addition product, probably SO_4, was collected in small amounts along with larger quantities of SO_2. The rate constant for this reaction was estimated to be $(5.6 \pm 0.6) \times 10^{-17}$ cc/molec-sec at 300°K at 2 torr pressure.

18. The SO_3-N atom reaction yielded SO_2 as a principal product. Rate constants for this reaction were found to be $(4.5 \pm 0.7) \times 10^{-16}$ and $(5.4 \pm 0.5) \times 10^{-16}$ cc/molec-sec when the reaction was terminated with NO and by low temperature trapping, respectively. The reaction was associated with an activation energy of about 2.3 kcal/mole in the temperature range 300

to 523°K. It is suggested that an addition complex, $SO_3.N$, may be formed in the primary step (corresponding to $SO_3.O$ in the O atom reaction), with rearrangement to form an intermediate from which stable products may emerge.

19. The reaction of SO_3 with nitrogen atoms was treated as a sequence of two competitive, consecutive, second order reactions, and the ratio, $K = k_{14}/k_{15}$, of the rate constants for the O atom and N atom reactions with SO_3 was calculated from the concentrations of O and N atoms in every experiment. By substitution of k_{14} (rate constant for the $SO_3 + O$ reaction, which was determined independently) into K, values of k_{15} were obtained which were in excellent agreement with the values of k_{15} based on the initial flow rates of the reactants and SO_2 produced. It was concluded that the results support the proposed mechanism,

$$SO_3 + N \longrightarrow SO_2 + NO$$

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

$$SO_3 + O \longrightarrow SO_2 + O_2$$

APPENDIX

As an incidental to the experiments in which SO was generated by the reaction of COS + O, a few observations were made on the behaviour of COS when it was admitted to active nitrogen from a microwave discharge. The reaction was accompanied by a blue flame in the vicinity of the COS inlet jet, and the almost instantaneous formation of a golden-yellow non-crystalline transparent product (presumably an S-N compound) that was deposited on the wall in the zone defined by the reaction flame. This product appeared to suffer no change in appearance when it was exposed for a prolonged period to a stream of active nitrogen.

Despite the blue reaction flame, the yellow nitrogen afterglow was still apparent at certain flow rates of COS. For such conditions, the reaction was stopped after a given reaction time by titrating out the residual N atom with NO. The data so obtained for several initial flow rates of COS and N atoms are shown in Table XXXV. From these data a rate constant was evaluated for the reaction on the assumption that the probable reaction products, CO and NS, did not react appreciably with atomic nitrogen. No justification for this assumption can be offered, since there is practically no information available about the reaction $NS + N \rightarrow N_2 + S$ (which might subsequently be followed by $S + COS \rightarrow CO + S_2$ and $S_2 + N \rightarrow NS + S$, etc.). Obviously, a much more detailed study of the system is required before more than order-of-

TABLE XXXV

REACTION OF CARBONYL SULPHIDE WITH ATOMIC NITROGEN

Microwave discharge system
Molecular nitrogen flow rate 250×10^{-6} mole/sec
Total pressure 2.5 torr
Reaction temperature 300°K
Reaction time 17.6 msec

COS input (mole/sec)$\times 10^{6}$	N atom flow (mole/sec)$\times 10^{6}$	N atom residual (mole/sec)$\times 10^{6}$	k (cc/molec-sec)$\times 10^{1}$
0.34	1.32	1.06	4.8
0.54	1.03	0.70	3.2
0.26	1.53	1.32	5.3
0.39	1.35	1.05	4.6
0.28	1.47	1.20	3.3
0.17	1.50	1.36	5.1
0.37	1.52	1.16	4.2

magnitude significance can be attached to the rate constant, perhaps by monitoring more than one reaction partner as a function of reaction time.

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