

THE REACTIVE SPECIES IN ACTIVE NITROGEN¹

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ABSTRACT

A study has been made of the discrepancy between the N-atom content of active nitrogen as inferred from the maximum HCN production from the reaction of many hydrocarbons, and that indicated by the extent of NO destruction. The HCN production from several hydrocarbons was similar at high reaction temperatures in a spherical reaction vessel, and was independent of reaction temperature in a cylindrical reaction vessel. The ratio (NO destroyed)/(HCN produced) was found to be independent of the mode of excitation of the molecular nitrogen and of the N-atom concentration, and to be unaffected by the addition, upstream, of N₂O or CO₂. Although NH₃ was found to be a minor product of the hydrocarbon reactions, HCN accounted for at least 96% of the N-atom content of the products under conditions where its formation is considered a measure of the N-atom concentration. The NO "titration" value, the maximum extent of HCN production from C₂H₄, and the destruction of NH₃ after different times of decay of active nitrogen gave evidence that part of the NO reaction occurred, as does the NH₃ reaction, with excited nitrogen molecules. The long lifetime of the N₂* species capable of reaction with NO or NH₃, as calculated from the above data, strongly favors its identification as low vibrational levels of the N₂(A³Σ_g⁺) molecule. A consideration of the values for the NO/HCN, NH₃/HCN, and NH₃/NO ratios, after different times of decay, for poisoned and unpoisoned systems, suggested that the N₂* responsible for the NH₃ reaction is formed only during homogeneous recombination of N atoms, while the N₂* responsible for reaction with NO might be produced by wall recombination as well. Possible reactions of excited molecules present in the active nitrogen - NO system that might lead to decomposition of NO without consumption of N atoms are discussed.

INTRODUCTION

Although the chemical activity of active nitrogen appears to be due mainly to ground-state atoms (1), recent work indicates that excited molecules (2-5) might be important in at least some active nitrogen reactions. For example, there seems little doubt that the reaction of active nitrogen with NH₃ involves excited molecules (6-8). Verbeke and Winkler have also suggested (9) that the greater nitrogen atom content of active nitrogen indicated by the NO titration (10), in comparison with that inferred from the maximum production of HCN from ethylene, may be due to reaction of NO with excited nitrogen molecules, in addition to its very rapid reaction with nitrogen atoms. On the other hand, the discrepancy between the two estimates of nitrogen-atom concentration has been attributed (11, 12) to the complexity of the hydrocarbon reaction.

The destruction of NH₃ in measurable amounts has only been detected in active nitrogen produced by a condensed discharge (6, 9, 13) and it has been suggested (14) that this reaction occurs with a species that is produced only by this mode of excitation of the molecular nitrogen. It has been reported (14) that, in active nitrogen produced by a microwave discharge, the maximum yield of HCN and the NO titration technique both indicate the same nitrogen-atom concentration.

The purpose of the present work was twofold: (i) to examine more closely the discrepancy between the two chemical methods of estimating the nitrogen-atom concentration of active nitrogen, (ii) to study the relative extents of reaction of active nitrogen, after

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different times of decay, with reactants that appear to involve mainly nitrogen atoms (e.g. C_2H_4), excited molecules (e.g. NH_3), or both (e.g. NO). Some of these interrelations have been examined previously as a function of pressure (13) and, in a preliminary way, as a function of decay of active nitrogen (9), but not as a function of time of decay of active nitrogen under controlled reaction conditions.

An investigation was first made of the effect of the shape of the reaction vessel on the temperature dependence of HCN production from hydrocarbons, in the region where this was independent of flow rate of the hydrocarbon, in active nitrogen produced by a condensed discharge and by a microwave system. Many of the preliminary results of the present investigation were reported at the Symposium on Some Fundamental Aspects of Atomic Reactions held at McGill University, Montreal, September 6 and 7, 1960.

EXPERIMENTAL

Nitrogen, nitric oxide, ammonia, and the hydrocarbons used were purified by methods similar to those described in previous papers from this laboratory. Nitrous oxide and carbon dioxide were freed from water by distillation at $-78^\circ C$.

The products of the reactions with hydrocarbons were trapped at liquid air temperature and distilled into an absorber that contained ice at liquid air temperature, and the aqueous solution analyzed after the absorber had been allowed to warm to room temperature. The amount of NH_3 in the products was estimated by titration with standard sulphuric acid, and this was followed by analysis for hydrogen cyanide by standard silver nitrate titration, in the presence of added ammonia, with potassium iodide as indicator. Ammonia was also qualitatively identified among the reaction products by infrared spectroscopy. Cyanogen has been shown, by previous workers, to be present in relatively insignificant quantities.

Excess NH_3 from the ammonia reaction was analyzed in the same way as the ammonia content of the products from the hydrocarbon reactions.

The products from the nitric oxide reaction consisted of nitric oxide and nitrogen dioxide (generally present as N_2O_3) and these were trapped quantitatively at about $-210^\circ C$, using liquid nitrogen under reduced pressure. Nitric oxide was separated, with a Toepler pump, from the nitrogen dioxide, maintained at $-64^\circ C$, and the amount of each gas was measured by pressure-volume methods at constant temperature. This technique gave good agreement with that used by Verbeke and Winkler (9). The reaction of nitric oxide with active nitrogen was also followed by the gas phase titration method (10).

The reactions of active nitrogen with nitrous oxide and carbon dioxide were followed by trapping unreacted nitrous oxide, or carbon dioxide, at liquid air temperatures and estimating their amounts by pressure-volume methods at constant temperature. No other products were observed, even with a trap at $-210^\circ C$.

The experiments described in this paper were made in two different types of apparatus, (I) and (II). To increase the reproducibility in the experiments, both types of apparatus were equipped with a stopcock between the reaction vessel and products trap. This minimized contamination of the reaction vessel and discharge regions by reaction products. Kel-F stopcock grease was used and was unaffected by active nitrogen. To obtain reproducible results, it was also necessary to operate the condensed discharge, in either apparatus, for at least 15 minutes prior to initiating a reaction.

Apparatus (I) was similar to that used by previous workers (6, 9, 13). The reaction vessels were of unpoisoned pyrex and the dimensions were varied in several of the experiments. Condensed and microwave discharges were used as alternative methods of obtaining active nitrogen. The condensed discharge operated between aluminum electrodes, 45 cm apart, and at a flash rate of about 10 sec^{-1} . The microwave discharge operated at 2450 Mc/sec and was supplied from a Raytheon 125-watt generator. The flow rate of molecular nitrogen, at a pressure of 2.45 mm Hg, was 133×10^{-6} mole/sec.

Apparatus (II) utilized a condensed discharge to produce a high concentration of nitrogen atoms, to facilitate the study of possible reactions of excited nitrogen molecules, which are probably produced by the recombination of nitrogen atoms (13). A large bulb was incorporated into the center of the discharge tube to reduce "pulsing" in the active nitrogen stream. The reaction vessel was a straight, pyrex tube of 25-mm diameter, which contained two fixed reactant jets, about 14 and 14.5 cm below the discharge tube. It was also provided with a mobile reactant jet that could be moved from 0.1 to 45 cm below the lower of the two fixed jets, by a stopcock arrangement (15) that provided a friction drive on the lower part of the mobile jet column. This column contained a glass-encased thermocouple, which permitted a measurement of temperature 3.0 cm below the outlet of the mobile jet. Both the fixed upper jets, and the mobile jet, contained six small holes placed symmetrically around their bulbous ends to produce an even flow of reactant into the active nitrogen stream.

All experiments in apparatus (II) were made in an unheated reaction vessel and at a pressure of 3 mm of Hg. The flow rate of molecular nitrogen was 378×10^{-6} mole/sec, corresponding to a linear flow rate of

478 cm/sec. Experiments were made in both an unpoisoned reaction vessel, and in the reaction vessel poisoned by water vapor ($<0.03 \times 10^{-6}$ mole/sec), introduced through a capillary leak into the molecular nitrogen before the discharge. This minute amount of vapor apparently has no measurable effect (16) on the course of the active nitrogen reactions but does poison the walls of the apparatus effectively against the decay of nitrogen atoms.

RESULTS

A Comparison of the Maximum Extent of Reaction of Active Nitrogen with Nitric Oxide and with Hydrocarbons

The extent of the reaction with NO was taken as the initial flow rate of NO minus the flow rate of total nitrogen oxides (i.e. NO+NO₂) analyzed in the products. Hydrogen cyanide production was taken as a measure of the reaction of nitrogen atoms with ethylene, ethane, *n*-butane, and but-2-ene. At the maximum extent of these reactions, the total of ammonia and cyanogen in the products never exceeded 4% of the hydrogen cyanide.

In Table I are shown the data obtained, using apparatus (I), when variations were made in reaction temperature, dimensions of the reaction vessel, and type of discharge

TABLE I
Reaction of active nitrogen with nitric oxide compared with production of HCN from hydrocarbons

Reaction vessel	Discharge	Total press., mm Hg	Temp., °C	Hydrocarbon	Max. HCN produced, mole/sec ($\times 10^6$)	Max. NO consumed, mole/sec ($\times 10^6$)	Ratio NO/HCN
A. Sphere, 85 mm i.d.	Condensed	2.45	50	C ₂ H ₄ , <i>n</i> -C ₄ H ₁₀ , C ₄ H ₈	5.0	12.4	2.5
			440	"	7.75	12.4	1.6
Sphere, 85 mm i.d.	"	2.45	50	C ₂ H ₆	2.2*	12.4	5.6
			440	"	7.4	12.4	1.7
B. Cylinder, 20 mm i.d.	"	2.45	40	C ₂ H ₄ , <i>n</i> -C ₄ H ₁₀	6.8	11.2	1.7
			400	"	7.2	11.2	1.6
C. Sphere, 110 mm i.d.	"	2.45	50	C ₂ H ₄	2.2	4.0	1.8
			440	"	2.6	4.0	1.5
D. Sphere, 110 mm i.d.	"	2.45	50	C ₂ H ₄	1.5	2.6	1.7
			440	"	1.5	2.6	1.7
E. Sphere, 85 mm i.d.	Microwave	2.45	80	C ₂ H ₄	1.4	2.4	1.7
			440	C ₂ H ₄ , C ₂ H ₆	1.4	2.4	1.7
F. Cylinder, 20 mm i.d.	"	2.45	80	C ₂ H ₄	1.3	2.2	1.7
			440	"	1.3	2.2	1.7
G. Cylinder, 20 mm i.d.	"	3.70	110	C ₂ H ₄	1.9	3.8	2.0
			440	"	1.9	3.8	2.0

*The HCN yield from ethane at 50° C never reached a true limiting value.

used to produce the active nitrogen. Values for NO consumption obtained by product analysis agreed well with results obtained by the gas phase titration with NO at the lower atom concentrations, but at higher atom concentrations (systems A and B) the titration gave results that were 10–20% lower than those reported in the table.

The Production of Ammonia from the Reaction of Active Nitrogen with Ethylene and Ethane

The relative amounts of HCN and NH₃ produced in these reactions in a spherical, unpoisoned reaction vessel, with a condensed discharge, are shown in Table II. Production of ammonia from *n*-butane and but-2-ene was found to be similar to that from ethylene at both temperatures.

TABLE II
Production of NH_3 in the reaction of active nitrogen with C_2H_4 and C_2H_6

Reactant flow rate	Reaction of ethylene				Reaction of ethane			
	at 50° C		at 440° C		at 50° C		at 440° C	
	HCN	NH_3	HCN	NH_3	HCN	NH_3	HCN	NH_3
1.0*	1.3	0.02	1.3	0.18	0.6	0.02	0.9	0.15
2.2	2.4	0.03	—	—	0.9	0.04	—	—
2.8	—	—	3.0	0.26	—	—	3.2	0.18
4.0	2.8	0.03	—	—	—	—	—	—
6.9	—	—	4.1	0.05	—	—	3.9	0.05
14.8	3.0	0.03	4.2	0.04	1.1	0.05	4.2	0.03
22.7	3.0	0.03	4.2	0.03	1.3	0.05	4.2	0.03

*All units are mole/sec $\times 10^{-6}$.

The Influence of Nitrous Oxide and Carbon Dioxide on the Reactions of Active Nitrogen with Nitric Oxide and Ethylene

Apparatus (I) was used, with a reaction vessel consisting of two spherical bulbs, connected by a 10-cm pyrex tube of 20-mm i.d. Nitrous oxide or CO_2 entered the active nitrogen in the upper bulb (85-mm i.d.), while NO or C_2H_4 was admitted to the lower bulb (110-mm i.d.). A condensed discharge activated the nitrogen, and the vessel walls were not poisoned.

The admission of either N_2O or CO_2 to the active nitrogen in the upper vessel caused no significant change in the heat given off at any position in the system. Both N_2O and CO_2 were destroyed to a minor extent; the N_2O destruction appeared to increase with reaction temperature. The addition of these gases to the active nitrogen resulted in an increase in the maximum extents of reaction of both NO and C_2H_4 , but the ratio $\text{NO}_{\text{consumed}}/\text{HCN}_{\text{produced}}$ remained essentially unchanged over a range of flow rates of N_2O or CO_2 from 2×10^{-6} to 30×10^{-6} mole/sec. Typical results, for a flow rate of N_2O or CO_2 of 6.7×10^{-6} mole/sec, are shown in Table III.

TABLE III
Effect of N_2O and CO_2 on the reactions of active nitrogen with NO and C_2H_4

	Maximum extent of HCN production from ethylene, mole/sec ($\times 10^6$)	Maximum extent of decomposition of NO , mole/sec ($\times 10^6$)	Ratio NO/HCN
Without N_2O	3.7	6.3	1.7
With N_2O	4.2	7.1	1.7
Without CO_2	3.6	6.4	1.8
With CO_2	4.4	7.7	1.7

A Comparison of the Plateau Values for HCN Production from C_2H_4 and of NH_3 Destruction and NO Destruction, after Different Times of Decay of Active Nitrogen

Apparatus (II) permitted the accurate determination of these plateau values (maximum extents of reaction) at four different levels, spaced 15 cm apart, of the mobile jet under otherwise similar conditions. These levels corresponded to 31.4, 62.7, and 94.3 milliseconds of decay of active nitrogen after the reference level, 0.1 cm below the lowest fixed jet. The temperature increases in the active nitrogen stream at these same positions were also determined before the reactant was introduced. The extent of NO destruction was estimated, at the different levels, by a visual gas phase titration (10). Since the results

obtained in apparatus (I) indicate that the HCN plateau values are independent of reaction temperature in a cylindrical vessel, and this has recently been confirmed by other workers (17) for the ethylene reaction, these values are considered to be a measure of the maximum HCN production from ethylene. Good linear relations, of which those in Fig. 1 are typical, were obtained between the plateau values for the reactions and the

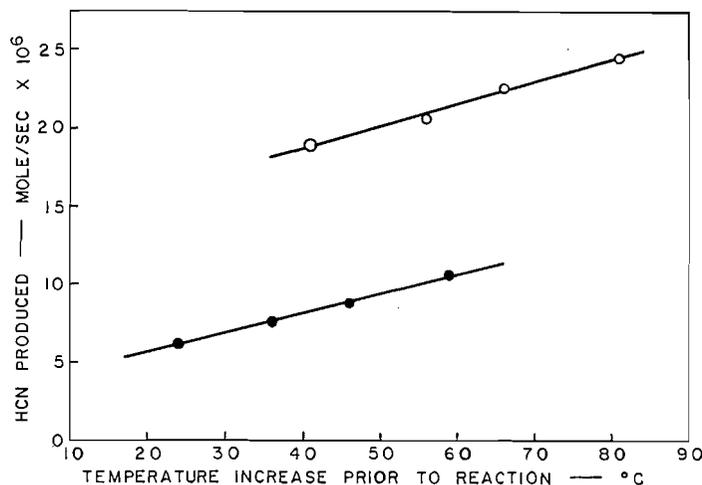


FIG. 1. Plot of HCN produced from ethylene against the temperature of the active nitrogen, above room temperature: ○, poisoned system; ●, unpoisoned system.

temperature increases in the active nitrogen in both the poisoned and unpoisoned systems. Unfortunately, the possibility of estimating the relative concentrations of active nitrogen from such relative temperature increases is applicable only to a given apparatus and given operating conditions. For example, for a temperature increase of 46° C prior to reaction, the destruction of NH_3 , or production of HCN from C_2H_4 , in the poisoned system, was more than double, while NO destruction was slightly less than double that observed in the unpoisoned system. Presumably, the condition of the system determines the N-atom concentration upstream, hence the extent of formation of excited nitrogen molecules, and both of these, in turn, may be reflected in the observed temperature increases and plateau values for the reactions.

A plot of NH_3 destroyed against HCN produced from C_2H_4 , at the different levels in the reaction tube, is linear for both the poisoned and unpoisoned systems (Fig. 2). Extrapolation of the line for the unpoisoned system to zero HCN production gives an intercept on the axis of NH_3 destruction of 0.2×10^{-6} mole/sec, while a similar extrapolation of the line for the poisoned system gives an intercept on the axis of HCN production of 11×10^{-6} mole/sec.⁴

The ratios (NH_3 decomposed/HCN produced), (NO decomposed/HCN produced), and (NH_3 decomposed/ NO decomposed), more simply referred to hereafter as the ratios NH_3/HCN , NO/HCN , and NH_3/NO , all decrease, at constant pressure, with time of decay of the active nitrogen in the poisoned system, while in the unpoisoned system the ratio NO/HCN increases markedly, and the ratio NH_3/HCN increases slightly. Verbeke

⁴Extrapolation to zero value of HCN production yields values corresponding to reaction conditions where the N-atom concentration has fallen to a very low value, i.e., to long distances downstream. Of course, the extrapolated values are applicable only to the present system, wherein a large N-atom concentration existed upstream, and a relatively high concentration of excited nitrogen molecules may then exist at a distant position downstream, as a result of N-atom recombination upstream.

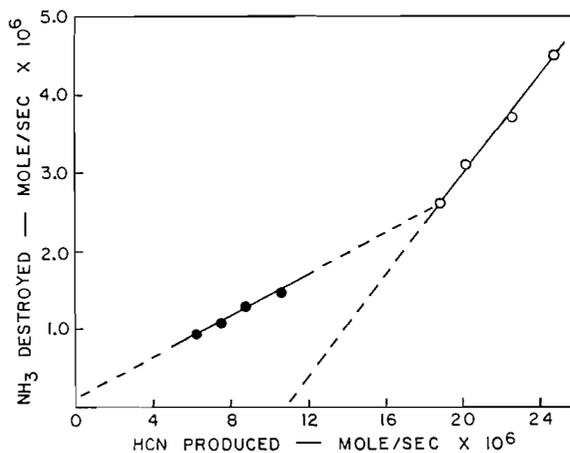


FIG. 2. Plot of NH_3 destroyed against HCN produced from C_2H_4 at the different levels: ○, poisoned system; ●, unpoisoned system.

and Winkler (9) had some indication of an increase in the NO/HCN ratio with decay time in a poisoned system.

Reasonably good straight lines are obtained if plots are made of NH_3/HCN against HCN (Fig. 3A), NO/HCN against HCN (Fig. 3B), and NH_3/NO against NO (Fig. 4)

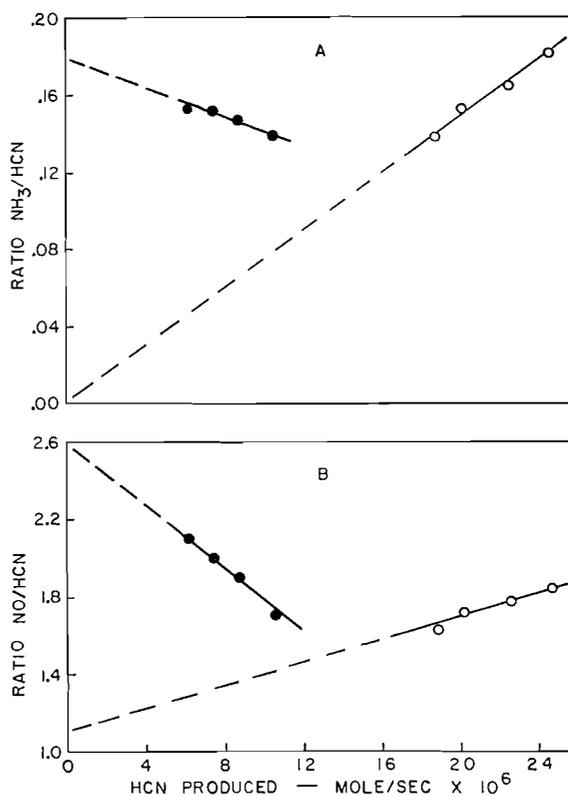


FIG. 3. (A) Plot of ratio NH_3 destroyed/HCN produced; (B) plot of ratio NO destroyed/HCN produced: ○, poisoned system; ●, unpoisoned system.

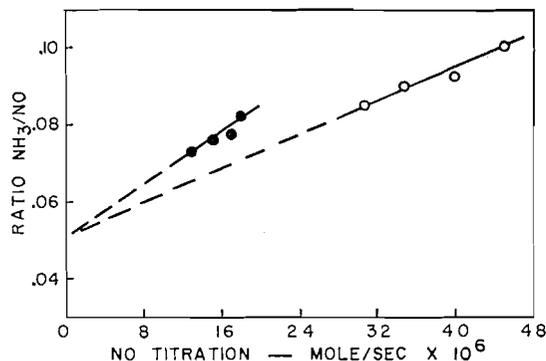


FIG. 4. Plot of ratio NH_3 destroyed/ NO destroyed against NO titration value at the different levels: \circ , poisoned system; \bullet , unpoisoned system.

for different levels in the reaction tube. Extrapolation of these, as indicated in the figures, are certainly not accurate, but it is apparent that the lines of Fig. 3 are of opposite slopes for the poisoned and unpoisoned systems, and extrapolate to widely different intercepts, while the lines in Fig. 4 are of similar slope and extrapolate to similar values for the two systems. The significance of these relations will be discussed later.

Effect of Adding NH_3 Upstream from NO , C_2H_4 , or NH_3 ; and C_2H_4 above NH_3

The experiments were made in apparatus (II).

(a) Effect of Adding NH_3 above NO

Since both the reactions of NO and NH_3 may be due, at least in part, to the reaction of excited nitrogen molecules, the addition of one upstream might be expected to decrease the extent of the reaction of the other. However, when NH_3 was introduced at a flow rate of 4.0×10^{-6} mole/sec through the fixed upper jet, the change in the end point of the NO titration was negligible in the poisoned system at all levels down to 45 cm. If anything, there was a slight increase in the end point, especially at the 45-cm level. In the unpoisoned system, the increase in the end point was more significant, e.g., 3.7×10^{-6} mole/sec at the 30-cm level, when NH_3 was added at a flow rate of 2.2×10^{-6} mole/sec.

(b) Effect of Adding NH_3 above C_2H_4

If the reaction of NH_3 with active nitrogen involves N atoms in any way, the HCN production from C_2H_4 might be expected to decrease when NH_3 is added upstream. In fact, addition of NH_3 at the fixed upper jet slightly *increased* the HCN production from C_2H_4 over that obtained at the various levels and flow rates when no NH_3 was added upstream. This increase was larger in the unpoisoned system. The results are given in Table IV.

In the poisoned system, the C_2H_4 reaction temperature at the 45-, 30-, and 15-cm levels, in the presence of NH_3 , was about 3°C higher than in its absence, while, in the unpoisoned system, the corresponding increase was about 8°C at all three levels. In the unpoisoned system, an increase in the intensity of active nitrogen afterglow was observed at the lower levels, upon the introduction of the NH_3 .

The addition of C_2H_4 downstream from NH_3 was found to decrease the extent of NH_3 decomposition and this decrease became larger as the C_2H_4 was added closer to the NH_3 jet. Since the addition of an excess of C_2H_4 below NH_3 appeared to terminate the NH_3 active nitrogen reaction, this method has been used (18) to obtain a rate constant for the NH_3 reaction.

TABLE IV
Effect of addition of NH_3 on HCN production from C_2H_4

Level at which C_2H_4 added, cm	C_2H_4 flow rate, mole/sec ($\times 10^6$)	NH_3 flow rate, mole/sec ($\times 10^6$)	Increase in HCN production, mole/sec ($\times 10^6$)
Poisoned system			
45	52	2.5	2.1
45	60	"	2.4
30	52	2.5	1.4
30	60	"	1.4
15	52	2.5	1.5
15	60	"	0.4
15	60	8.0	2.7
0	46	2.5	0.4
0	60	"	1.7
0	60	11.7	2.1
Unpoisoned system			
45	46	2.5	3.9
45	"	7.7	4.2
30	46	2.5	4.5
15	46	2.8	2.6

(c) *Effect of Adding C_2H_4 above NH_3*

In the poisoned system, no decomposition of NH_3 was observed, after accounting for the slight NH_3 production from the C_2H_4 reaction, when 8.0×10^{-6} mole/sec of NH_3 was added at the 15- and 30-cm levels and 46×10^{-6} mole/sec of C_2H_4 added at the fixed upper jet. The extent of HCN production from the C_2H_4 reaction was slightly decreased. It may be noted that, at the 15-cm level, NH_3 was added in the region of the active nitrogen - C_2H_4 reaction flame, while at the 30-cm level, no reaction flame was visible.

(d) *Effect of Adding NH_3 above NH_3*

Ammonia was added through the fixed upper jet at flow rates lower than those corresponding to the plateau for destruction of NH_3 . Most of the NH_3 that was added was therefore destroyed above the 30-cm level. If excited molecules, capable of destroying NH_3 , were formed only during the decay of nitrogen atoms, in the presence of NH_3 , the addition of excess NH_3 at the lower positions should result in a total NH_3 destruction almost equal to that obtained when the excess is added at the fixed upper jet. However, for successive additions in the poisoned system, the combined extent of NH_3 destruction was 0.5×10^{-6} mole/sec less at the 30-cm level, and 1.0×10^{-6} mole/sec less at the 45-cm level, than when a flow rate of NH_3 in the plateau region, e.g., 8.0×10^{-6} mole/sec, was added at the fixed upper jet. In the unpoisoned system, the total extent of NH_3 destruction was approximately the same (1.5×10^{-6} mole/sec) whether the reactant was introduced at the upper level only, or at both upper and lower levels.

DISCUSSION

Essentially equal yields of HCN from hydrocarbons have been obtained in apparatus (I), as follows: ethylene, *n*-butane, but-2-ene, and ethane at elevated temperatures in a spherical reaction vessel, and ethylene and *n*-butane in an unheated cylindrical reaction vessel. The maximum HCN production from the hydrocarbons, except from C_2H_6 , does not vary, to any extent, with reaction temperature in a cylindrical vessel, with active nitrogen produced by either a condensed or microwave discharge. Consequently, any

uncertainty about having reached an HCN plateau that is independent of reaction temperature is eliminated, and there appears to be added justification for assuming that this value of HCN production corresponds to the N-atom concentration in the system. The reasons for the temperature dependence of HCN production observed in the present work, and in many previous studies (see, for example, ref. 13), in a spherical reaction vessel are not obvious, and further study of this problem is in progress.

The observed discrepancy between the estimations of active nitrogen concentration from NO destruction and from maximum HCN production, as reflected in the NO/HCN ratios of Table I, agrees well with that obtained previously (9) at similar reaction pressures, for active nitrogen produced by a microwave discharge: a value of about 1.7 at 2.45 mm, compared with a previous value of 1.6 at 2 mm, and a value of 2.0 at 3.7 mm, compared with the earlier value of 1.9 at 4.0 mm. Contrary to recent assumptions (19), the present data confirm the previous conclusion (9) that the NO/HCN ratio does not change appreciably with active nitrogen concentration at a constant total pressure, nor does it depend upon the mode of excitation of the nitrogen.

The lower N-atom concentration indicated by the extent of HCN production from hydrocarbons apparently cannot be due to the formation of N-containing products, other than HCN, in these reactions, since the total content of N atoms in the form of NH_3 or $(\text{CN})_2$ recovered from the hydrocarbon reactions, under conditions of maximum HCN production, is less than 4% of that recovered as HCN.⁵

Similarly, it seems unlikely that the discrepancy between the NO and HCN estimates of atomic nitrogen concentration is due to catalyzed recombination of N atoms on the parent hydrocarbon, after initial formation of a complex of relatively long life (20),



since the NO/HCN ratio would then be temperature dependent, and possibly also dependent on the N-atom concentration (13). No dependence of the ratio on temperature was observed in a cylindrical reaction vessel (Table I), while, in the unpoisoned system of apparatus (II), the ratio *increased* (Fig. 3B) with decreasing N-atom concentrations after longer decay times of the active nitrogen.

Again, the suggestion of Zinman (11) that the formation of a complex of a substantial lifetime might explain the pressure dependence (9) of the NO/HCN ratio also appears untenable. In modified form, his scheme may be represented by



Reaction [3'] is necessary since the reaction of N atoms with free radicals, which may conserve spin, is probably faster (21) than the N-atom reaction with the parent hydrocarbon. If it is assumed that the NO titration measures the N-atom concentration, this mechanism gives

$$\frac{[\text{NO consumed}]}{[\text{HCN produced}]} = \frac{[\text{N}]}{[\text{HCN}]} = \frac{nk_3 + k_4[\text{M}]}{nk_3}, \quad [5]$$

⁵The yield of NH_3 from the C_2H_4 reaction in the unheated spherical reaction vessel (Table II) was a considerable fraction of the slight HCN yield. However, there is considerable evidence, as will be discussed in a later paper, that this reaction involves excited nitrogen molecules at low reaction temperatures.

where n = number of carbon atoms in the hydrocarbon. On this basis, the NO/HCN ratio should depend on the molecular weight of the hydrocarbon, which is not borne out by the experiments described in Table I. Furthermore, experiments in apparatus (II) indicated that the NO/HCN ratio increased with time of decay of the active nitrogen in the unpoisoned system. Since the ratios involved plateau values for HCN production at the various levels for constant pressure conditions, an explanation for the discrepancy represented by the NO/HCN ratio must involve more than its pressure dependence.

Finally, it should be emphasized, perhaps, that a discrepancy, similar to that given by the NO/HCN ratio, has been observed when the active nitrogen concentration, estimated by the NO titration, was compared with the extent of reaction of active nitrogen with NO₂ (9) and, more recently, by the extent of its reaction with O₂, as given by the production of O atoms (22).⁶ Among the widely different chemical methods studied, therefore, the NO reaction, whether followed by gas phase titration or by analytical methods, appears to be unique in indicating an exceptionally high atomic nitrogen concentration.

The observation that the NO/HCN ratio does not have a fixed value, even at a given pressure, but depends on the time of decay of the active nitrogen, suggests (since the HCN data are based on plateau values) that the extent of the NO reaction does not vary directly with the N-atom concentration, but involves excited molecules derived from atom recombination or directly from the discharge tube. This is suggested also by the similarity in the plots of NH₃/HCN and NO/HCN against HCN yield for the poisoned and unpoisoned systems (Fig. 3), since the NH₃ reaction is known to involve excited molecules. Again, the similarities in slopes of the NH₃/NO plots against NO (Fig. 4), for both the poisoned and unpoisoned systems, and in the extrapolation of the lines to a similar low value, strongly suggest that both reactions occur, at least in part, with species produced by a similar mechanism.

Since the NO/HCN ratio may increase with time of decay of the active nitrogen, it is not likely that NO reacts with some species of long life, other than N atoms, that may be produced in a particular type of discharge. Moreover, most of the excited species that might be produced during the excitation process are known to be of short life (2, 23), and can be expected to decay rapidly with time. If an excited molecular species is responsible for part of the NO reaction, it is probably formed during the recombination of N(⁴S) atoms. The decrease in the NO/HCN ratio with decay of the active nitrogen in the poisoned system may then be explained if the disappearance of N atoms in this system, which occurs at about twice the rate of the homogeneous recombination, is considerably slower than that of any N₂* which might have been produced, mostly upstream in the region of relatively high N-atom concentration.⁷ The same seems also to be true for the N₂* that reacts with NH₃ in a poisoned system, since it appears, from the extrapolation in Fig. 2, that the decomposition of NH₃ falls to zero at rather high values of the N-atom concentration in such a system. In contrast, in the unpoisoned system, the extrapolated value for NH₃ destruction at zero HCN production suggests a considerable concentration of N₂* in this system, even under conditions where the N-atom concentration has fallen to a low value. The small limiting extent of NH₃ destruction suggests further that N₂* is produced during the relatively small homogeneous part of the overall decay of N atoms in the unpoisoned system.

⁶It might be noted, however, that the analysis of O-atom concentration in this reaction by the NO₂ titration recently indicated a N-atom concentration similar to that inferred from the NO titration (12).

⁷This explanation suggests that a system poisoned with metaphosphoric acid (9) corresponds more closely with an unpoisoned system than with a system poisoned with H₂O vapor. For O atoms, at least, small amounts of water vapor have been shown (24) to be a most effective poison against surface recombination.

The difference in slopes and intercepts (Fig. 3A) when the NH_3/HCN ratios are plotted against HCN, for the poisoned and unpoisoned systems, may also be explained if the N_2^* responsible for NH_3 decomposition is formed by homogeneous recombination and persists in significant concentrations, in the unpoisoned system, into the regions where the N-atom concentration has fallen to low values. The much higher extrapolated value of 2.6 for the plot of NO/HCN against HCN (Fig. 3B) in the unpoisoned system suggests that some N_2^* capable of NO destruction may be formed by wall decay of N atoms. The corresponding extrapolated value of 1.1 in the poisoned system indicates that the concentration of N_2^* responsible for NO destruction becomes negligible when the N-atom concentration has decreased to a very low value in this system.

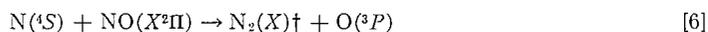
In view of the preceding discussion, it seems reasonable to conclude that NO is destroyed not only by N atoms, but also by an excited molecular species of considerable lifetime produced by both homogeneous and surface decay of N atoms. The destruction of NH_3 , on the other hand, appears to be due only to an excited molecule produced during homogeneous decay.

Nature of the Excited Molecular Species that might React with NO

A vibrationally excited, ground-state nitrogen molecule might contain sufficient energy to cause dissociation of NO during a collision process, and, at least in the lower vibrational levels, would be expected to be of long life (23, 25, 26). Quite high vibrational levels of the ground state may be populated directly by homogeneous recombination of N atoms, as pointed out by Polanyi (27) for atomic association reactions of this type. To contain sufficient energy to cause dissociation of NO after a collision of the Second Kind, the molecule would have to be in at least the 27th vibrational level (9). There is some experimental evidence (28) for the presence, in active nitrogen, of $\text{N}_2(X^1\Sigma_g^+)$ in vibrational levels as high as the 27th, but they would presumably be deactivated readily by collision processes because of their small vibrational level spacing. It is improbable, therefore, that such molecules would be present in sufficient concentration to account for the NO/HCN ratios.

Another possibility is that such molecules are produced in the excitation process. Kaufman and Kelso (25) found that the addition of N_2O or CO_2 removed energy from certain species, probably ground-state molecules in low vibrational levels, in active nitrogen emanating from a microwave discharge. In the present studies, the addition of either gas to discharged nitrogen made little difference to the NO/HCN ratio (Table III). Moreover, there was negligible temperature increase when these gases were introduced into active nitrogen formed in a condensed discharge, compared with that observed (25) in active nitrogen from a microwave discharge. This suggests that microwave excitation may be more effective than a condensed discharge in producing excited ground-state molecules of low-energy content, and that, if NO reacts with excited nitrogen molecules, as well as atoms, the N_2^* are certainly of higher energy than those removed by collision with N_2O or CO_2 .

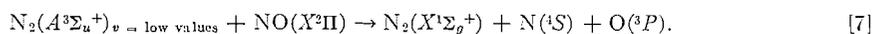
Production of vibrationally excited, ground-state molecules might be expected to be favored, through spin coupling (29) with the paramagnetic NO molecule, in the reaction



in a manner analogous to that found for other reactions of atoms with molecules (e.g. ref. 30). In fact, there is evidence that this reaction does produce nitrogen in low-lying levels of the ground state (25). However, it is exothermic only to the extent of about 75 kcal, and the maximum energy that might be expected to remain as vibrational energy

in the newly formed bond would be between about 53 kcal, corresponding to $v = 8$ (31), and 75 kcal, corresponding to $v = 12$ (27). Hence, although reaction [6] occurs at almost the bimolecular collision rate (12, 32), and would provide vibrationally excited molecules almost immediately after the introduction of NO, such molecules could not directly decompose NO.

On the other hand, $N_2(A^3\Sigma_u^+)$, in the first or second vibrational levels, would have sufficient energy to decompose NO in a collision of the Second Kind. Such a molecule may be formed directly by recombination of N atoms, or by a cascade process after the N atoms recombine into a higher state. Since its transition to the ground state, the only lower-energy state available, involves a change in spin (the forbidden Vegard-Kaplan bands), it has a relatively long radiative lifetime, recently estimated (33) to be between 0.24 and 50 second. It has also been shown (23) that, although vibrational levels of the A state higher than $v = 1$ lose their energy in a number of collisions much less than 10^8 , the $v = 1$ level can survive 10^9 collisions. Moreover, there is the possibility of a resonance energy transfer between low vibrational levels of the A -state molecule and NO, as pointed out previously (9). For these several reasons, it is suggested that NO might be decomposed in the following process, which may conserve spin:



It should be noted that, although the A -state molecule has recently been observed in absorption (34, 35), no direct evidence is available that its concentration in active nitrogen is sufficient to account for the NO/HCN discrepancy. There is little question, however, that its concentration is much greater than that of the B -state molecule, or other triplet-state molecules such as the precursor of the 'Y' bands in active nitrogen (36, 37), the $Y^3\Sigma_u^-$ (perhaps better referred to as the $B'^3\Sigma_u^-$ (38, 39)) state, or of the $^3\Delta_u$ state, all of which probably have very short lifetimes (33, 8). Process [7] is therefore favored over the analogous process, for which evidence has been obtained by Heath (40),



Heath observed that the active nitrogen afterglow, especially transitions from $v = 5, 6,$ and 7 levels of the B state, was weakened at higher pressures (10 to 760 mm) in the presence of NO. He suggested, therefore, a resonance energy transfer in process [8], which conserves spin and may lead to the dissociation of NO, to explain the disappearance of the First Positive group in high-pressure air discharges. The $^4\Sigma^-$ state for NO correlates with the dissociation limit (41, 42) for NO into $N(^4S) + O(^1D)$.

The Lifetimes of the Excited Molecules Involved in the NO and NH₃ Reactions

The plateau values for NO and NH₃ destruction, after different times of decay of the active nitrogen, permit calculation of lifetimes for the excited molecular species that appear to be involved in these reactions, provided the rate constant of surface decay of the N atoms is known for the given experimental conditions. This was obtained, for the present study, from the equation

$$-d[N]/dt = k_1[N] + k_2[N]^2P, \quad [9]$$

where $k_1[N]$ represents the rate of heterogeneous decay, and $k_2[N]^2P$ represents the rate of homogeneous decay of N atoms. The value of k_2 may be taken to be 3×10^{-33} cc² molecule⁻² sec⁻¹ (43, 44).⁸ Values of $[N]$ were inferred from maximum HCN yields in the

⁸This value was based on a N-atom concentration deduced from HCN production from C₂H₄ or C₂H₆ at high reaction temperatures, and consequently could be too high if values of $[N]$ so obtained were too low.

C₂H₄ reaction at various levels, and values of $d[N]/dt$ were obtained as slopes of the straight-line plots of HCN production against decay time of the active nitrogen at the 0-, 15-, and 30-cm levels (-1.57×10^{16} and -1.00×10^{16} molecules cc⁻¹ sec⁻¹ respectively in the poisoned and unpoisoned systems). The following reasonable values of k_1 (sec⁻¹) were obtained:⁹

Level, cm	Poisoned system	Unpoisoned system
0	1.4	3.5
15	1.7	4.4

The rate of decay of the N₂* species, assumed capable of causing the decomposition of NO in reaction [7], may be represented by

$$d[N_2^*]/dt = \frac{1}{2}ak_2[N]^2P + \frac{1}{2}bk_1[N] - k_3[N_2^*], \quad [10]$$

from which,

$$k_3 = \frac{k_1[N]}{2[N_2^*]} + \frac{k_2[N]^2P}{2[N_2^*]} - \frac{d \ln [N_2^*]}{dt}. \quad [11]$$

The first term on the right-hand side of equation [10] represents the rate of production of N₂* by homogeneous recombination, the second term its rate of possible production by heterogeneous recombination, and the last term its decay. The concentration of molecular nitrogen is approximated by the total pressure, P , in the system. Equation [11] is derived by arbitrarily taking the values of the constants a and b to be unity. This is a reasonable value for a if, for example, N₂* represents the A state of nitrogen, since this state may be populated directly during the volume decay of N atoms, as well as from the end result of light emission in the First Positive system. Although the value of b is much more uncertain, the recent work of Harteck, Reeves, and Mannella (4, 48) supports the possibility that an excited molecular species may be formed during surface recombination.

Values of $d \ln [N_2^*]/dt$ were obtained from plots of $\ln \frac{1}{2}(\text{NO} - \text{HCN})$ against time, on the assumption that $[N_2^*] = \frac{1}{2}(\text{NO}_{\text{reacted}} - \text{HCN}_{\text{produced}})$. Values of k_1 , k_2 , and $[N]$ were taken as outlined previously, and the following values for k_3 were obtained:

$$\begin{aligned} k_3 &= 7.9 \text{ sec}^{-1}, \text{ poisoned system at 0-cm level;} \\ &= 9.7 \text{ sec}^{-1}, \text{ poisoned system at 15-cm level;} \\ &= 8.3 \text{ sec}^{-1}, \text{ unpoisoned system at 15-cm level.} \end{aligned}$$

Accordingly, the excited state of N₂, assumed capable of reacting with NO, is calculated to have a half-life, assuming its decay to be a first-order process, of about 8.4×10^{-2} second. This value is somewhat higher than the minimum lifetime of 10^{-2} second observed by Lichtin (49) and the value of 2.6×10^{-2} second recently observed by Wilkinson and Mulliken (50), but less than the value of 0.15 second inferred by Carleton (34), for the $v = 0$ level of the N₂($A^3\Sigma_u^+$) molecule. (The A state contains 142 kcal/mole of excess energy and low-lying vibrational levels of this electronic state would contain sufficient energy, 150 kcal/mole, to cause reaction [7].)

⁹If values for k_1 are similarly calculated from the NO data, it is found that the value for the unpoisoned system (2.1 sec^{-1}) agrees well with that (2.5 sec^{-1}) previously reported (45) for such a system, but a larger, not a smaller, value is obtained for the poisoned system. If the larger value of k_2 obtained by other investigators (46, 47) from the NO titration are substituted into equation [9], along with the present NO data, the anomaly is accentuated. This suggests that the N-atom concentrations inferred from the NO titration are too high.

The extents of NH_3 destruction at different levels enable a similar calculation of the rate constant, k_4 , for the decay of the N_2^* species capable of destroying NH_3 . However, recent measurements (18) on the rate of the active nitrogen - NH_3 reaction have given further indication that the N_2^* responsible for the NH_3 reaction is formed only during homogeneous decay of N atoms, in which case $b = 0$ in equations [10] or [11]. The values obtained for k_4 (sec^{-1}) are then:

Level, cm	Poisoned system	Unpoisoned system
0	10.6	6.7
15	9.6	7.3

The average value in the poisoned system of 10.1 sec^{-1} indicates a half-life for the N_2^* species of 6.9×10^{-2} second.

It is interesting, perhaps, that there is a definite trend towards higher values of the ratio of N_2^* responsible for NO destruction, given by $\frac{1}{2}(\text{NO} - \text{HCN})$, to N_2^* responsible for NH_3 reaction, given by the extent of NH_3 destruction, at greater times of decay of the active nitrogen in the unpoisoned system:

Level, cm	Poisoned system	Unpoisoned system
0	2.24	2.52
15	2.35	3.15
30	2.32	3.24
45	2.23	3.58

This gives further evidence that NO may react with a N_2^* species produced at the wall as well as in volume decay of N atoms.

The Behavior of Reactions in the Presence of NH_3 , N_2O , and CO_2

Herron *et al.* (14) have observed that the addition of NH_3 to active nitrogen produced by a microwave discharge, in which the destruction of NH_3 was immeasurably small, did not affect the value of the NO titration. The significant *increase* in the NO titration, observed in the present studies, when NH_3 was added to the unpoisoned system, may be attributed to a slower decay of N atoms in the presence of the polar NH_3 molecule, which may serve as a poison against the wall recombination of N atoms. Consequently, if NO reacts with N_2^* , it would seem that the N_2^* involved is different from that responsible for the decomposition of NH_3 , or, that the products of the NH_3 decomposition react rapidly with NO. The latter alternative is quite possible, since Bamford has shown (51) that NO rapidly scavenges NH_2 radicals, even at room temperature, according to



Moreover, the reaction



occurs (52) during the photolysis of NH_3 in the presence of NO, and in NH_3 flames (53), together, perhaps, with the reaction



Since the addition of NH_3 upstream from C_2H_4 did not decrease the extent of HCN production (Table IV), the reaction of NH_3 with active nitrogen apparently does not consume N atoms. The slight increase in HCN production in the poisoned system is

difficult to explain, but might be due to additional wall poisoning by NH_3 . The greater increase, proportionately, in HCN production in the unpoisoned system is almost certainly due to the efficient wall poisoning by small amounts of NH_3 in this system. The increased temperature of the C_2H_4 reaction, in both systems, in the presence of added NH_3 , may then be explained by more extensive reaction in the presence of the higher N-atom concentration promoted by the poisoning effect of NH_3 . The poisoning effect of NH_3 might also account for the visual increase in the afterglow intensity *downstream* when small amounts of NH_3 were added upstream in the unpoisoned system. A decrease in light intensity in the region where a low flow rate of NH_3 is added, accompanied by an increase at points further downstream in the unpoisoned system, has recently been confirmed quantitatively by measurements (54) with a photomultiplier tube. Since the total destruction of NH_3 was not affected by addition of small amounts of NH_3 upstream in the unpoisoned system, the slower decay of N atoms, due to NH_3 absorption on the walls, appears to compensate for any loss of N_2^* effective for the NH_3 reaction resulting from a low NH_3 concentration in the region between the fixed and mobile jets.

The small increase in HCN production from C_2H_4 , and in the extent of NO decomposition, in the presence of N_2O or CO_2 (Table III), might also be attributed to poisoning of the walls against atom recombination by these molecules in the unpoisoned system of apparatus (I). This wall effect might also provide an explanation for the enhanced afterglow intensity observed downstream by Kaufman and Kelso (25) when N_2O was added upstream. These authors attributed the higher N-atom concentration downstream to a decreased rate of homogeneous recombination of N atoms in the region of higher temperature produced upstream by the absorption of energy by N_2O from excited nitrogen molecules of relatively low energy content. However, the rate of homogeneous recombination of N atoms has a small temperature dependence (14), and, although the temperature coefficient of this association reaction has generally been considered to have a negative value (55), there have been some indications (43, 44) that it may even have a small positive value.

Since no NH_3 decomposition was observed when C_2H_4 was added upstream, it is apparent that C_2H_4 may remove the N_2^* responsible for the NH_3 reaction. This is not surprising, in view of the many degrees of freedom of the ethylene molecule. However, although an excited C_2H_4 molecule formed during a collision of the Second Kind with N_2^* might suffer some decomposition, such fragments would consume N atoms (1) before producing HCN. In the opinion of the authors, the direct formation of HCN from hydrocarbons through chemical reaction with N_2^* is considerably less probable than the decomposition of NO induced by N_2^* .

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