

THE REACTION OF NITROGEN ATOMS WITH HYDROGEN ATOMS¹

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ABSTRACT

The reaction has been studied in a fast-flow system by the addition of atomic hydrogen to active nitrogen. Hydrogen atom concentrations were estimated from the maximum destruction of hydrogen bromide in the atomic hydrogen stream. The nitrogen atom consumption, in the reaction mixture, was determined by addition of nitric oxide at different positions along the reaction tube. A lower limit of $4.87 \pm 0.8 \times 10^{14}$ cc²mole⁻²sec⁻¹ was derived for the rate constant of the reaction of nitrogen atoms with hydrogen atoms, over the pressure range 2.5 to 4.5 mm, in an unheated reaction tube, poisoned with phosphoric acid. No reaction between nitrogen atoms and molecular hydrogen was observed, even at 350° C.

INTRODUCTION

A good deal of recent work has provided evidence for the existence, in the gas phase, of radicals consisting of nitrogen and hydrogen, e.g., NH, NH₂, N₂H₂, N₂H₃. Most of these have been identified spectroscopically from studies on such substances as hydrazoic acid, hydrazine, and ammonia (1, 2, 3). The failure of many investigators (4, 5) to find NH radicals, by mass spectrometry, in the dissociation of hydrazoic acid, has been attributed to the ability of the NH radical to abstract hydrogen atoms from chemically stable molecules, without the need for any activation energy. On the other hand, the presence of atomic nitrogen and hydrogen in the reaction products has suggested that nitrogen atoms are more or less passive toward bound hydrogen (4). From chemical studies, Winkler and his co-workers (6, 7) have similarly concluded that nitrogen atoms do not abstract hydrogen atoms in their attack on hydrocarbons or ammonia.

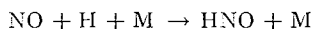
An attempt has been made in the present investigation to establish the kinetics and mechanism of the reaction that occurs in a mixture of nitrogen and hydrogen atoms.

EXPERIMENTAL

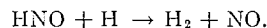
The apparatus was a fast-flow system, similar to that used in other studies in this laboratory. Microwave generators (Raytheon 125-watt diathermy unit, operating at a frequency of 2400 Mc/sec) were used to produce atomic nitrogen in one, and atomic hydrogen in a second, quartz discharge tube, each of which was of 12-mm i.d., and 10 cm long. The reaction vessel was a pyrex tube of 20-mm i.d., and 30 cm long, poisoned with 20% phosphoric acid. Five small inlets were placed along the reaction tube at different distances.

Nitrogen and hydrogen, after passage through liquid air traps, were passed into their respective discharge tubes and the emerging gas streams, containing nitrogen and hydrogen atoms, were blended in the reaction vessel. The nitrogen atom consumption, in the reaction mixture, was determined by addition of pure nitric oxide at subsequent jet positions along the reaction tube.

Nitric oxide reacts with hydrogen atoms by the termolecular mechanism (8, 9)



followed by



Hence, destruction of nitric oxide should occur only as a result of attack by active nitrogen, which permits the nitric oxide titration (10, 11) to be used for estimation of the nitrogen atom flow rate in the presence of hydrogen atoms.

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Hydrogen atom concentrations at the point of mixing were determined, for the same pressure and flow conditions that prevailed during the reaction, but without the nitrogen discharge in operation, by introducing excess hydrogen bromide, and estimating the maximum amount of hydrogen bromide consumed by hydrogen atoms (12). Hydrogen bromide flow rates, and unreacted hydrogen bromide, were estimated by condensing it in a removable trap containing standard NaOH solution, and back titrating the excess alkali with standard acid.

All the experiments were made in an unheated reaction tube, with the one exception that the reaction of nitrogen atoms with molecular hydrogen was studied at temperatures up to 350° C.

RESULTS AND DISCUSSION

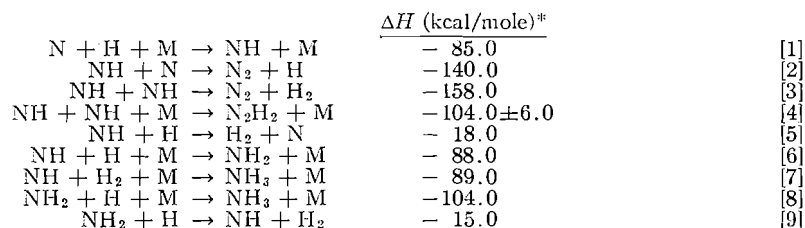
A series of experiments was first made in which molecular hydrogen was added to active nitrogen. No product was found from this reaction, and the afterglow intensity was unaffected (except for a possible dilution effect), even at high flow rates of molecular hydrogen, and at temperatures up to 350° C. This observation agrees with that from earlier studies by Kistiakowsky and Volpi (13) and Steiner (14), but is contrary to the results of Varney (15), who found small amounts of ammonia.

The reaction of nitrogen atoms with hydrogen atoms appeared to produce only small amounts of a basic substance, estimated by titration with standard acid. This product was assumed to be ammonia, since hydrazine, if formed, should react rapidly with either nitrogen or hydrogen atoms, which were present in excess in the gas stream (16). Moreover, earlier studies indicate that hydrazine is not a significant product of the reaction (1, 17). The data for ammonia production, in Table I, are in substantial agreement with earlier observations (1, 17).

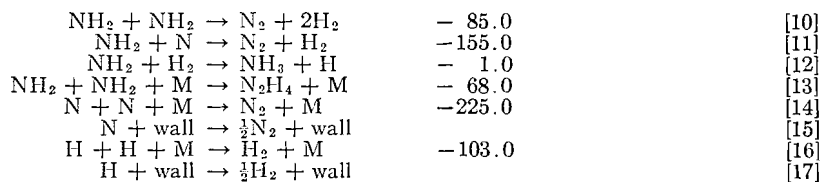
TABLE I
Ammonia produced in the reaction of nitrogen atoms with hydrogen atoms
(Unheated reaction tube poisoned with phosphoric acid)

Nitrogen pressure, mm	Hydrogen pressure, mm	Total pressure, mm	Nitrogen atom flow rate, mole/sec $\times 10^6$	Hydrogen atom flow rate, mole/sec $\times 10^6$	Ammonia produced, mole/sec $\times 10^6$
2.0	0.50	2.50	2.84	5.2	—
2.5	0.50	3.00	3.25	5.2	—
2.0	0.75	2.75	2.84	7.1	0.054
1.5	1.00	2.50	1.60	8.6	0.013
1.0	1.00	2.00	0.73	8.6	0.027
2.0	1.00	3.00	2.84	8.6	0.027
3.0	1.00	4.00	4.34	8.6	0.027
3.5	1.00	4.50	5.29	8.6	0.027

The following energetically favorable elementary reactions may be involved in a mixture of nitrogen atoms and hydrogen atoms:



*The heats of reaction are approximate, based on the data $D_{N-N} = 225$ kcal, $D_{H-H} = 103$ kcal, $D_{N-H} = 85$ kcal (18), $D_{H-NH} = 88$ kcal (19), $D_{H-NH_2} = 104$ kcal (20), $D_{HN-NH} = 104 \pm 6$ kcal (4); but they do indicate the energetics of the reactions considered.



The NH₂ can be formed only by reaction [6] which, followed by reactions [8] and [12], would lead to the formation of ammonia. The very small amount of ammonia produced (Table I) indicates that NH₂ exists in the gaseous mixture only in small amounts, in accordance with its formation from ternary collisions (reaction [6]), and its destruction by the probable reactions [9], [10], [11], and [13]. For a kinetic treatment, reaction [6], and the other termolecular reactions [4], [7], and [8], may be neglected in comparison with the bimolecular reactions [2], [3], and [5]. Reactions [9] to [13], inclusive, may then also be neglected, since they depend upon reaction [6].

From reactions [1], [2], [5], [13], and [15],

$$-d(N)/dt = k_1(M)(H)(N) + k_2(NH)(N) - k_5(NH)(H) + k_{14}(M)(N)^2 + k_{15}(N). \quad [18]$$

Reaction [2], the attack of NH by N, is probably very fast, since it appears to be quite analogous to the reaction of NO with N, for which a rate constant between 10⁻¹⁰ and 10⁻¹¹ cc molecule⁻¹sec⁻¹ (21, 22) has been found in recent investigations. No similar basis seems to be available for estimating the rate of reaction [5]. It is quite conceivable that it, too, might be a fast reaction, but there is no reason to suppose that its rate would exceed that of reaction [2], under the conditions of the present experiments.

If it is assumed that the rates of reactions [2] and [5] are equal,

$$-d(N)/dt = k_1(M)(H)(N) + k_{14}(M)(N)^2 + k_{15}(N). \quad [19]$$

On the other hand, if it is assumed that reaction [5] may be neglected relative to reaction [2], application of the steady-state approximation to NH yields

$$d(NH)/dt = k_1(M)(H)(N) - k_2(NH)(N) - k_3(NH)^2 = 0.$$

Since the NH concentration is expected to be small (the half-life of NH is about 9 × 10⁻⁴ second (1), compared with a value of approximately 10⁻² second for CH and CH₂), the term k₃(NH)² may be neglected. Then

$$k_1(M)(H)(N) = k_2(NH)(N)$$

and

$$-d(N)/dt = 2k_1(M)(H)(N) + k_{14}(M)(N)^2 + k_{15}(N). \quad [20]$$

Calculation from equation [20] should therefore give a lower limit for the value of k₁, which, however, is not likely to be in error by more than a factor of two.

If the wall recombination of nitrogen atoms is neglected, since the reaction of nitrogen atoms with hydrogen atoms has been studied at pressures higher than 2.5 mm (23, 24, 25), the rate expression is given by

$$-d(N)/dt = 2k_1(M)(H)(N) + k_{14}(M)(N)^2.$$

Upon integrating,

$$\ln \frac{(N)_0}{(N)_t} = 2k_1(M) \int_0^t (H) dt + k_{14}(M) \int_0^t (N) dt. \quad [21]$$

The rate expression for the decay of hydrogen atoms in reactions [16] and [17] is

$$-d(H)/dt = k_{16}(M)(H)^2 + k_{17}(H).$$

This integrates to

$$\ln \frac{(H)_0}{(H)_t} - \ln \frac{[k_{17} + k_{16}(M)(H)_0]}{[k_{17} + k_{16}(M)(H)_t]} = k_{17}t$$

or

$$(H)_t = \frac{k_{17}}{k_{16}(M)} \frac{1}{\left[1 + \frac{k_{17}}{k_{16}(M)(H)_0}\right] e^{k_{17}t} - 1}.$$

Hence,

$$\int_0^t (H)_t dt = \frac{1}{k_{16}(M)} \ln \left[1 + \frac{k_{16}(M)(H)_0}{k_{17}} (1 - e^{-k_{17}t})\right]. \quad [22]$$

Similarly, the nitrogen atom concentration at time t (reaction [14]) is given by

$$(N)_t = \frac{(N)_0}{k_{14}(M)(N)_0t + 1}$$

or

$$(N)_t dt = \frac{(N)_0 dt}{k_{14}(M)(N)_0t + 1}.$$

Upon integrating,

$$\int_0^t (N)_t dt = \frac{1}{k_{14}(M)} \int_0^t \frac{d[k_{14}(M)(N)_0t + 1]}{k_{14}(M)(N)_0t + 1} = \frac{1}{k_{14}(M)} \ln [k_{14}(M)(N)_0t + 1]. \quad [23]$$

Substitution of [22] and [23] in equation [21] yields the expression

$$k_1 = \frac{k_{16}}{2} \frac{\log \frac{(N)_0}{(N)_t} - \log [1 + k_{14}(M)(N)_0t]}{\log \left[1 + \frac{k_{16}(M)(H)_0}{k_{17}} (1 - e^{-k_{17}t})\right]}, \quad [24]$$

where $(N)_0$ = initial nitrogen atom concentration, $(H)_0$ = initial hydrogen atom concentration, $(N)_t$ = nitrogen atom concentration at time t , t = reaction time. The rate constant of reaction [16] was taken as $k_{16} = 10^{16} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ (26, 27) with $\gamma = 2 \times 10^{-5}$ (28), which, for the conditions used, corresponds to $k_{17} = 2.5 \text{ sec}^{-1}$. For the rate constant of reaction [14], the value of $k_{14} = 1.04 \times 10^{16} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ (25) was used.

Rate constants for the reaction of nitrogen atoms with hydrogen atoms under various conditions, derived from equation [24], on the assumption that atoms and molecules are equally effective as third bodies, are recorded in Table II. The average value of k_1 may be taken as

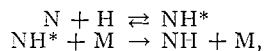
$$k_1 = 4.87 \pm 0.8 \times 10^{14} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$$

over the range of pressures from 2.5 to 4.5 mm, in an unheated reaction tube poisoned with phosphoric acid.

TABLE II
Rate constants for the reaction of nitrogen atoms with hydrogen atoms as a function of reaction time, pressure, and initial reactant concentrations (Unheated reaction tube poisoned with phosphoric acid)

Nitrogen pressure, mm	Hydrogen pressure, mm	Total pressure, mm	Nitrogen flow rate, mole/sec $\times 10^6$	Hydrogen flow rate, mole/sec $\times 10^6$	Total flow rate, mole/sec $\times 10^6$	M_1 , mole/sec $\times 10^6$	$(N)_0$, mole/cc $\times 10^{19}$	$(H)_0$, mole/cc $\times 10^9$	$\log \frac{(N)_0}{(N)_t}$	t , sec $\times 10^2$	k_1 , cc/mole ² -sec ⁻¹ $\times 10^{-11}$
2.0	0.50	2.50	133	44.5	177.5	1.38	2.21	3.91	0.0400	2.69	4.40
"	"	"	"	"	"	"	"	"	0.0659	4.48	5.65
"	"	"	"	"	"	"	"	"	0.0897	6.04	6.30
"	"	"	"	"	"	"	"	"	0.1209	7.50	5.50
Average $k_1 = 5.46$											
2.0	0.75	2.75	133	74.0	207.0	1.47	2.01	5.04	0.0417	2.54	5.75
"	"	"	"	"	"	"	"	"	0.0641	4.23	4.80
"	"	"	"	"	"	"	"	"	0.0841	5.70	5.00
"	"	"	"	"	"	"	"	"	0.1011	7.09	4.55
Average $k_1 = 5.02$											
2.0	1.00	3.00	133	95.0	228.0	1.60	2.00	6.03	0.0417	2.52	4.00
"	"	"	"	"	"	"	"	"	0.0659	4.20	3.34
"	"	"	"	"	"	"	"	"	0.0859	5.66	3.90
"	"	"	"	"	"	"	"	"	0.1109	7.03	5.05
Average $k_1 = 4.08$											
2.5	1.00	3.50	172	95.0	267.0	1.87	2.27	6.03	0.0540	2.51	4.19
"	"	"	"	"	"	"	"	"	0.0851	4.18	4.18
"	"	"	"	"	"	"	"	"	0.1140	5.63	4.62
"	"	"	"	"	"	"	"	"	0.1353	6.99	3.87
Average $k_1 = 4.22$											
3.0	0.50	3.50	219	44.5	263.5	1.87	3.22	3.69	0.0728	2.51	6.25
"	"	"	"	"	"	"	"	"	0.1143	4.24	5.75
"	"	"	"	"	"	"	"	"	0.1452	5.71	5.15
"	"	"	"	"	"	"	"	"	0.1771	7.09	5.60
Average $k_1 = 5.67$											
3.0	0.75	3.75	219	74.0	293.0	2.00	3.10	4.81	0.0728	2.45	4.57
"	"	"	"	"	"	"	"	"	0.1143	4.08	4.50
"	"	"	"	"	"	"	"	"	0.1452	5.48	4.10
"	"	"	"	"	"	"	"	"	0.1771	6.81	4.46
Average $k_1 = 4.41$											
3.0	1.00	4.00	219	95.0	314.0	2.14	2.95	5.85	0.0776	2.44	5.75
"	"	"	"	"	"	"	"	"	0.1256	4.06	6.50
"	"	"	"	"	"	"	"	"	0.1575	5.47	5.65
"	"	"	"	"	"	"	"	"	0.1842	6.79	4.82
Average $k_1 = 5.68$											
3.5	1.00	4.50	235	95.0	330.0	2.40	3.80	6.25	0.1075	2.61	4.50
"	"	"	"	"	"	"	"	"	0.1577	4.35	4.34
"	"	"	"	"	"	"	"	"	0.2116	5.86	5.35
"	"	"	"	"	"	"	"	"	0.2435	7.28	3.60
Average $k_1 = 4.45$											
Average $k_1 = 4.87 \pm 0.8 \times 10^4$ cc ² mole ⁻² sec ⁻¹											

The number of termolecular collisions may be calculated, using the collision model, and assuming the mechanism of the reaction to be



as given by

$$Z_{\text{ter}} = Z_{\text{NH}}Z_{\text{NH}^*.\text{M}}\tau_{\text{NH}^*},$$

where Z_{NH} and $Z_{\text{NH}^*.\text{M}}$ are the binary collision frequencies between N and H and NH^* and M respectively, and τ_{NH^*} is the mean life time of the complex NH^* . For $T = 300^\circ \text{K}$; $\text{M} = \text{N}_2$; collision diameters $\sigma_{\text{N}} = 2.95 \text{ \AA}$, $\sigma_{\text{H}} = 2.4 \text{ \AA}$, $\sigma_{\text{NH}} = 2.68 \text{ \AA}$; and $\tau_{\text{NH}^*} = 10^{-13}$ second,

$$Z_{\text{ter}} = 1.2 \times 10^{16} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1},$$

and for $\text{M} = \text{H}_2$, and $\sigma_{\text{H}_2} = 2.7 \text{ \AA}$,

$$Z_{\text{ter}} = 9.2 \times 10^{15} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}.$$

Thus, the reaction of nitrogen atoms with hydrogen atoms has a probability factor of 4×10^{-2} or 5×10^{-2} depending on whether nitrogen or hydrogen is considered as a third body.

The value of k_1 reported here for the three-body interaction of nitrogen and hydrogen atoms is lower than that found for many atom-combination reactions, but, within experimental error, it probably should be regarded as comparable with the value of $1.83 \times 10^{15} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ found recently for the rate constant of the analogous reaction of nitrogen and oxygen atoms (25), and with the most recent value, $1.0 \times 10^{15} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$, for the rate constant of the $\text{O} + \text{O} + \text{M}$ reaction (29).

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