

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE REACTIONS OF HYDROGEN ATOMS WITH HYDRAZINE AND WITH AMMONIA

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Introduction

The reactions of hydrogen atoms with ammonia and hydrazine which are reported on here, represent two of the possible reactions involved in the formation of ammonia and hydrazine from nitrogen and hydrogen atoms.¹ In order to obtain a valid mechanism for the modes of formation, it is necessary to have experimental data concerning the interaction of either hydrogen or nitrogen atoms with ammonia or hydrazine. The effect of nitrogen atoms (from active nitrogen) on ammonia is very small.² The reaction of hydrogen atoms with ammonia was studied semi-quantitatively by Boehm and Bonhoeffer³ and no reaction was observed; but, since the result is of importance experimentally and theoretically, the experiments have been repeated with greater accuracy. Elgin and Taylor⁴ showed that, in the photosensitized decomposition of hydrazine by mercury in the presence of hydrogen, hydrogen atoms and hydrazine must react and subsequently produce ammonia. Since the completion of the present experiments, Wiig and Kistiakowsky⁵ have published the results of careful experiments on the photochemical decomposition of ammonia, in which use is made of the reaction of hydrogen atoms on hydrazine to account for the low quantum yield of the ammonia decomposition. In the present case this was the primary reaction studied, the method of production of the hydrogen atoms and the conditions being quite different from either of the above investigations.

Experimental Procedure and Apparatus

Materials.—Hydrogen from a tank was saturated with water and passed into the apparatus without further purification. Liquid ammonia was stored in a tank over metallic sodium. Gas from this tank was absorbed completely in water. Hydrazine hydrate was prepared from c. p. hydrazine hydrochloride by adding strong potassium hydroxide solution to the solid hydrochloride at 0–10°. The potassium chloride formed was filtered off and the hydrazine hydrate (with water) was dehydrated with solid potassium hydroxide. Dehydration was carried out in a vacuum by distilling the hydrazine through a series of traps containing solid potassium hydroxide, always at less than 50°. Analysis of the liquid obtained showed that it contained over 85% hydrazine.

Analyses.—Ammonia was determined by titration with standard sulfuric acid (*ca.*

¹ Steiner, *Z. Elektrochem.*, **36**, 807 (1930).

² Dixon and Steiner, *Z. physik. Chem.*, **B17**, 327 (1932).

³ Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

⁴ Elgin and Taylor, *THIS JOURNAL*, **51**, 2059 (1929).

⁵ Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

0.25 or 1.00 *n*). Hydrazine, when present alone, was determined by either of two methods, titration with sulfuric acid (0.25 *n*) or by titration with standard potassium iodate solution (0.25 *m*) according to the directions of Kolthoff.⁶ Ammonia and hydrazine, when present together in a solution, were determined as follows: the sum of hydrazine plus ammonia in one-half of the solution by titration with sulfuric acid and the hydrazine in the other half by the potassium iodate method. Ammonia was found by difference. The method was checked by analyzing mixtures containing known amounts of hydrazine and ammonia and proved to be accurate to better than one per cent.

Apparatus.—The type of apparatus employed was similar to that previously described.² Hydrogen, ammonia and hydrazine were admitted to the apparatus through capillaries. The hydrazine flow rate was controlled by regulating the temperature of the hydrazine source and the flow rates of the other two gases by using various sized capillaries. In some cases the ammonia was heated before it entered the reaction tube by wrapping the inlet tube with nichrome ribbon for 15 cm. just before the point where connection was made with the reaction tube. The approximate temperature of the ammonia was determined by inserting a thermocouple junction at the connecting point to the reaction tube and standardizing at various currents in the nichrome coil. The hydrogen was activated in a 1.9 meter discharge tube by the current from a 3 k. v. a. transformer at 12,000 volts. The atoms from the discharge were pumped rapidly through a long reaction tube and through two traps. Connections from a McLeod gage were sealed in the reaction tube 8 cm. from the discharge and at the end. Ammonia or hydrazine was introduced into the reaction tube 16 cm. from the discharge (see Fig. 1). The traps were fitted with ground joints and cooled with liquid air. The outlet from the pumps was connected to a buret, so that the gases delivered could be collected and measured.

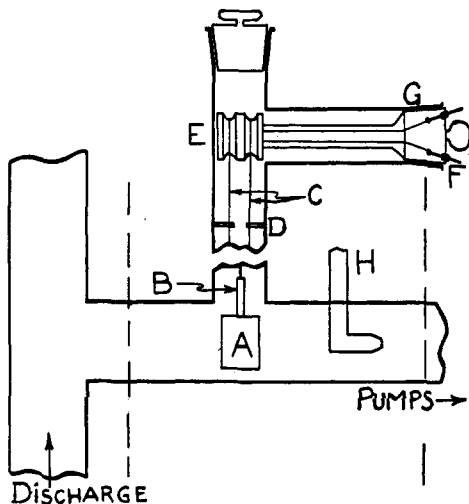


Fig. 1.—Calorimeter for measuring hydrogen atom concentrations.

The hydrogen atom concentrations were measured at a point 8 cm. from the discharge. The calorimetric method employed was similar to that which has been described by v. Wartenberg and Schultze⁷ and by Smallwood.⁸ It involved the measurement of the temperature rise of a known weight of platinum upon exposing the metal to the atom recombination for a definite length of time; 13.5 g. of sheet platinum were pressed into a flat unit to serve as a calorimeter, which is denoted by A in Fig. 1. A single copper-constantan thermocouple junction was inserted into the middle of the platinum and the leads were protected for two centimeters above the metal by a small platinum tube, B. The thermocouple leads, C, were guided by the glass rods, D, then passed over the grooved spool, E, and finally connected to the tungsten-glass seals at F. The calorimeter was raised or lowered by winding the thermocouple leads up or down on the

⁶ Kolthoff, *THIS JOURNAL*, **46**, 2009 (1924).

⁷ V. Wartenberg and Schultze, *Z. physik. Chem.*, **B6**, 261 (1930).

⁸ Smallwood, *THIS JOURNAL*, **51**, 1985 (1929).

spool. The platinum hung freely in the reaction tube when in use. The connection to the McLeod gage is not shown in Fig. 1; the NH_3 or N_2H_4 inlet is shown at H. The reaction tube was maintained at a constant temperature between the dotted lines, 25 cm., by means of water contained in a copper box. The potential difference between the thermocouple junctions was determined with the aid of a Leeds and Northrup "low voltage" Type K potentiometer. The thermocouple was standardized before use at 100° .

Procedure.—After conditions reached a steady state the pressure at the calorimeter and the volume of hydrogen delivered per minute were determined and the discharge turned off. The calorimeter was lowered and the electrical connections at F were made. When the temperature of the calorimeter reached some point (about 5° above the temperature of the water-bath) the discharge was turned on for a suitable length of time, then shut off, and the cooling curve for the calorimeter was measured. The procedure for measuring the amount of decomposition in the reactions was similar to that described previously,² the accuracy of the results being much higher. Under strictly comparable conditions the amounts of ammonia (or hydrazine) passing through the apparatus in unit time were determined with and without activation of the hydrogen. Determinations of the pressures, flow rates, atomic hydrogen concentration and analyses of the products collected in the traps were made. The difference between these experiments was a measure of the extent and course of the reaction.

Results

The Hydrogen Atom Concentrations.—The maximum temperature rise of the platinum upon exposing it to the hydrogen atoms was not a true measure of the heat of atom recombination. The radiation loss during the time necessary for the attainment of temperature equilibrium was sufficient to give a low value for the temperature rise. After cutting off the supply of atoms, the time-temperature curve of the metal was measured. When the cooling curve was extrapolated to the time when the atoms were "shut off," the corresponding temperature was that which the calorimeter would have attained if there had been no time lag in the heat exchange. The difference between the extrapolated final temperature and the initial temperature gave the uncorrected temperature rise for the known heating period. The radiation loss during the heating period was calculated from the average slope of the cooling curve between two temperatures and the time the calorimeter was in this temperature range. Adding the radiation loss to the uncorrected temperature rise gave the true value. The results of some experiments are summarized in Table I. The values of the temperature rise and the radiation loss correspond to the heating periods shown in the third column. The number of calories liberated per minute was the product of the temperature rise, the weight and the specific heat of the platinum;⁹ that is, $T \times 13.5 \times 0.0336$. The *percentage dissociation* of the hydrogen was calculated from the relation,

$$\% \text{ Dissociation of } \text{H}_2 = 100 \times \frac{T \times 13.5 \times 0.0336}{104,000 \times V}$$

⁹ "International Critical Tables," Vol. V, p. 93.

where 104,000 represents the heat of formation of one mole of hydrogen from the atoms and V the number of moles of hydrogen passing through the apparatus per minute.

TABLE I

HYDROGEN ATOM CONCENTRATIONS AS DETERMINED CALORIMETRICALLY					
Weight of platinum, 13.5 g. Pressure, 0.21–0.24 mm. Streaming velocity, 3.10–3.16 $\times 10^{-3}$ mole per minute					
Milliamperes in discharge	Temperature rise, millivolts	Time, seconds	Radiation loss, millivolts	Temperature rise per minute, °C.	% H ₂ Dissociation
30	1.70	42.0	0.53	76	11
50	1.93	23.0	.37	144	20
65	1.88	17.0	.27	182	25
65	2.05	18.0	.29	187	26
125	2.55	15.0	.25	268	37
125	2.23	14.0	.22	251	35
235	2.43	10.0	.16	389	54

The results of the experiments, as to the effects of pressure, temperature of the walls and current strength in the discharge, are similar to those obtained by previous investigators,^{8,10} and it is reasonably certain that the measured atomic concentrations were accurate to better than $\pm 10\%$, which was sufficient for the purposes intended.

The Reaction of Hydrogen Atoms with Hydrazine.—When hydrogen atoms were mixed with hydrazine, there was a reaction with formation of ammonia and some gases not condensed by liquid air. Much heat and a weak green fluorescence were liberated at and near the point where the hydrazine and hydrogen atoms mixed. The fluorescence increased in intensity as the hydrazine or hydrogen atom concentrations increased and ceased *immediately* upon shutting off the hydrogen discharge or hydrazine supply. Further investigation of the fluorescence is described below.

The reaction was investigated by finding the effect of the hydrogen atom and hydrazine concentrations upon the amount of hydrazine decomposition and amount of ammonia formed. The results of some experiments are summarized in Table II. The effect of temperature on the extent of reaction was determined by varying the temperature of the water-bath which surrounded the reaction tube. Although this bath did not control the temperature of the entire reaction tube, it did, however, extend well past the region where the heat and fluorescence were given out. The pressures shown in Table III are those measured in the absence of hydrazine. Adding hydrazine increased the pressure by about 0.05 mm. as a result of reaction, which increase would have decreased the hydrogen atom pressure even if there had been no reaction. No correction has been made for this change. Experiments made in the absence of hydrogen atoms are recorded in Table II, in which cases $p_{\text{H}} = 0$.

¹⁰ Wrede, *Z. Physik*, **54**, 53 (1929); Steiner and Wicke, *Z. physik. Chem.*, Bodenstein-Festband, 817 (1931).

TABLE II

THE REACTION OF HYDROGEN ATOMS WITH HYDRAZINE, SHOWING THE EFFECTS OF THE REACTION TEMPERATURE AND THE CONCENTRATIONS OF THE REACTANTS
 Streaming velocity without hydrazine, $3.1-3.2 \times 10^{-3}$ mole per minute

Expt.	$p_H + p_{H_2}$ mm.	p_H mm.	Reaction temp., °C.	Moles NH_3 $\times 10^3/\text{min.}$	Moles N_2H_4 $\times 10^3/\text{min.}$	% N_2H_4 dec.	Moles NH_3 Moles N_2H_4 dec.
3	0.23	0.14	22	0.317	0.085	77.4	1.06
4	.17	.00	22	.000	.377
5	.24	.12	22	.214	.117	68.1	0.86
6	.23	.10	22	.189	.155	57.8	.89
7	.18	.00	22	.000	.355
13	.21	.15	22	.257	.215	62.6	.72
14	.20	.00	22	.000	.574
15	.22	.12	22	.262	.276	54.0	.81
16	.23	.10	22	.218	.346	42.3	.86
17	.18	.00	22	.000	.625
18	.24	.17	0	.299	.238	60.8	.82
20	.24	.12	0	.257	.312	48.6	.87
21	.24	.10	0	.220	.361	40.5	.89
22	.23	.00	0	.000	.616
23	.21	.14	22	.076	.000	100.0	.67
24	.21	.00	22	.000	.112
25	.21	.11	22	.081	.000	100.0	.72
26	.21	.09	22	.089	.000	100.0	.79
32	.21	.07	22	.097	.000	100.0	1.05
33	.21	.00	22	.000	.092

TABLE III

THE EFFECT OF THE AMOUNT OF WATER ON THE DECOMPOSITION OF HYDRAZINE BY HYDROGEN ATOMS

p_H	Moles NH_3 $\times 10^3/\text{min.}$	Moles N_2H_4 $\times 10^3/\text{min.}$	% N_2H_4 decomposed	Moles NH_3 Moles N_2H_4 dec.	% H_2O in hydrogen
0.082	0.266	0.141	69.2	0.85	3
.080	.234	.120	71.0	.80	>5
.094	.248	.058	86.0	.70	>5
.081	.245	.056	86.5	.69	3

When Experiments 13-17 and 18-22 in Table II are compared, it is seen that a change in temperature had no appreciable effect on the amount of hydrazine decomposition or the amount of ammonia formed. For a constant initial hydrazine concentration the percentage decomposition of the hydrazine and amount of ammonia formed decreased as the atomic hydrogen concentration decreased (Experiments 3-7). It should be pointed out that the actual number of moles of hydrogen atoms was always about three to ten times in excess of the moles of hydrazine. If the hydrogen atom concentration was held constant and the initial hydrazine concentration decreased, the absolute amounts of hydrazine decomposed and ammonia formed decreased too, but the percentage decomposition of the hydrazine increased. This is not true, of course, in the cases where all

of the hydrazine decomposed (see Experiments 23-33). From some fifty experiments carried out it was found that the ratio of NH_3 formed to N_2H_4 decomposed was between 0.67 and 1.0. Although these ratios are not as accurate as desired, a consideration of all the experiments indicated that the ratio increased as the excess of hydrogen atoms over hydrazine decreased. It was possible that some ammonia passed through the first trap without condensing, since the mass velocity of the gases was three meters per second. Several experiments, yielding negative results, were made to see whether any ammonia might be collected in the second trap by cooling with liquid air.

The "streaming velocity," which was the amount of gas delivered by the pumps per minute, was determined with and without hydrazine added to the hydrogen atoms. The difference between these values gave the net number of moles of permanent gas, presumably nitrogen, formed during reaction. The accuracy of these measurements was ± 2 cc. per minute (25° and 760 mm.) $\sim 0.09 \times 10^{-3}$ moles per minute, which permits only certain general conclusions to be drawn from the results. The ratio of the moles of gas formed to the moles of hydrazine decomposed per minute varied between 1.0 and 1.9, the average ratio from all experiments being 1.3. In Experiment 3, for example, the increase in streaming velocity was 12 cc. per minute; hence there is no doubt that in some cases the ratio exceeded 1.0.

One objection to the method employed in the present work is that water was introduced into the hydrogen and the possibility arises that the dissociation products of water from the discharge may have initiated the reactions observed. This objection is shown to be incorrect in the light of the experiments given in Table III in which the amount of water in the hydrogen was varied. The first two and the last two experiments should be compared.

A slight modification of the apparatus permitted the observation of the fluorescence through a quartz window waxed on the reaction tube, the spectrograph being sighted down the tube to obtain greater light intensity. A Schmidt and Haensch spectrograph, with an average dispersion of 70 Å. per millimeter between 5000 and 6500 Å. was used for photographing in the visible portion of the spectrum. The longest exposure of ten hours of the fluorescence with Eastman Hypersensitized plates showed many lines (or bands) stretching from 4800 to 6200 Å. and, since proper precautions had been taken, these were not to be identified as the hydrogen molecular spectrum reflected from the discharge. The lines were so faint and, in most cases, diffuse that only approximate values of the wave lengths were found. In the region between $\lambda\lambda 5200$ -5700 Å. the wave lengths checked the strongest lines reported by Rimmer¹¹ for the so-called α -bands produced

¹¹ Rimmer, *Proc. Roy. Soc. (London)*, **A103**, 696 (1923).

in an ammonia flame. The Schuster bands at λ 5635 and 5670 were not observed. The matter may be of interest in connection with the production of these bands or, if the bands can be definitely attributed to some molecule, as a means of identifying one of the intermediates in the reacting system.

The Reaction of Hydrogen Atoms with Ammonia.—A summary of the results of some of the experiments on the reaction of ammonia and hydrogen atoms is given in Table IV. The temperatures recorded are those of the ammonia at the entrance to the reaction tube, the temperature of the reaction tube being 20–25° in all cases. The percentage of water in the hydrogen was approximately 6% in Experiment III and 3% in Experiments I and II.

TABLE IV
EXPERIMENTS SHOWING THE EFFECT OF HYDROGEN ATOMS ON AMMONIA
Ammonia pressure, 0.06 mm. Streaming velocity of H₂, 2.9–3.1 × 10⁻³ mole/minute

Expt.	$P_H + P_{H_2}$, mm.	P_H , mm.	Temp., of NH ₃ , °C.	Moles NH ₃ hr. × 10 ³	Amt. of decomp., %	% corrected
I 1	0.17	0.11	25	42.0	2.1	1.6
II 1	.18	.12	25	42.3	3.3	2.8
II 4	.20	.12	25	42.7	2.5	2.0
II 5	.20	.08	25	43.4	0.7	0.2
III 7	.19	.00	170	39.5
III 8	.18	.12	260	37.4	5.5	5.0
III 9	.18	.12	105	38.0	4.0	3.5
III 10	.17	.11	50	38.0	4.0	3.5
III 11	.16	.00	50	39.6

The distance from the discharge to the ammonia inlet was only 16 centimeters; consequently the decomposition observed may have been due in part to a diffusion of the ammonia back into the discharge, followed by dissociation. Since nitrogen from an uncondensed discharge has no effect on ammonia,² the former was admitted to the discharge in place of hydrogen and the amount of decomposition was measured in the usual way. The percentage decomposition observed was 0.5, so this amount was subtracted from the percentages observed with hydrogen in order to obtain the corrected values shown in the last column of Table IV. The experiments III did not indicate any significant increase in reaction as the temperature of the ammonia was raised to 260°. The following factors may have been important on heating the ammonia above 100°. The number of "high temperature" ammonia molecules reaching the reaction tube may have been too small to give any reaction or the heated ammonia made the glass surface active so that the hydrogen atoms recombined on the walls. Finally, the differences in amounts of decomposition in Experiments II and III may have been due to the difference in amounts of water present, for oxygen atoms (from the water) may have reacted with the ammonia and accounted for all the decomposition observed. Only about ten per cent.

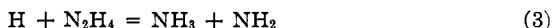
dissociation of the water, followed by reaction, will explain the results on this basis. The reaction of hydrogen and oxygen, initiated by the photochemical decomposition of ammonia, possesses an abnormal temperature coefficient and there is also evidence that ammonia or its dissociation products are involved in the reaction chains set up.¹² This suggested the possibility that ammonia was not reacting with hydrogen atoms, but with the dissociation products of water. As a basis for calculations, the percentage decomposition at 25° may be set equal to 3.0 at 25°, which is certainly an upper limit.

Discussion

The mechanism of the reaction of hydrogen atoms with hydrazine as given by Wiig and Kistiakowsky⁵ is as follows



The results of the present investigation agree with the above scheme in that approximately one mole of ammonia and one of permanent gas are produced for every mole of hydrazine decomposed. The observed decomposition of one mole of hydrazine led to more than one mole of permanent gas and less than one mole of ammonia, indicating that some side reaction, perhaps heterogeneous, destroyed some N_2H_3 . For example, $\text{H} + \text{N}_2\text{H}_3 = 2\text{H}_2 + \text{N}_2$ increases in rate as the hydrogen atom concentration increases, decreases the ammonia yield, and increases the yield of permanent gas above that expected, which is in accord with the results. Apart from a wall recombination of the hydrogen atoms, there is no explanation of the fact that the atom concentrations had to be ten times in excess of the hydrazine concentration in order to obtain total decomposition of the hydrazine. Several facts dealing with the photochemical decomposition of ammonia are of interest, since Equations (1) and (2) are involved in the mechanism. The over-all temperature coefficient of (1) and (2) was shown to be zero, hence the temperature coefficient of the quantum efficiency is not connected with these processes. The photochemical experiments of Gedye and Rideal,¹³ carried out by a flowing method, showed that hydrazine was produced in concentrations of 0.02 to 0.7 mm., but, in formulating the reaction mechanism, they did not consider reactions similar to (1) and (2).⁴ The reactions



will not account for the results of the experiments described here. If, in the mechanism of Wiig and Kistiakowsky for the photochemical de-

¹² Professor H. S. Taylor at Princeton kindly communicated these results before their publication, for which I wish to express my thanks.

¹³ Gedye and Rideal, *J. Chem. Soc.*, 1160 (1932). See also Koenig and Brings, *Z. physik. Chem.*, Bodenstein-Festband. 595 (1931)

composition of ammonia, (1) and (2) are replaced by (3) and (4), then, when there are no wall effects, one finds the quantum yield is independent of the light intensity and decreases as the pressure is raised. However, Reaction (4) must possess a temperature coefficient and the decomposition of one mole of hydrazine would lead to more than one mole of ammonia and less than one mole of permanent gas, which is not in accord with the results.

According to Steiner,¹ the formation of hydrazine from nitrogen atoms and hydrogen molecules takes place according to the reactions $N + H_2 = NH_2$ and $2NH_2 = N_2H_4$ in three-body collisions. A dissociation of the hydrogen, up to ten per cent., had little effect on the hydrazine yield, which would be understandable provided the hydrogen atoms had no effect on the hydrazine formed. However, Steiner's experiments show that the hydrazine pressures were of the order of 10^{-2} mm. and the hydrogen atom pressures 5×10^{-2} mm., hence the interaction between these two gases was considerable. Qualitatively, the results may be explained by postulating that nitrogen atoms decompose hydrazine into nitrogen and hydrogen (no ammonia was observed). Adding hydrogen atoms not only destroys hydrazine, but also nitrogen atoms, and the end result is an approximate constancy of the hydrazine yield. Since hydrogen and nitrogen atoms have little effect on ammonia, the yield of the latter increases as the concentrations of the former increase. The reaction¹⁴ $X + NH + NH_3 = N_2H_4 + X^*$ does not enter into consideration when only nitrogen atoms and hydrogen molecules are present; in other cases the stability of ammonia toward hydrogen atoms is an indication that ammonia is too stable to react with NH.

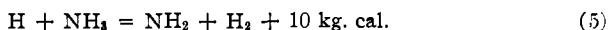
Koenig and Wagner¹⁵ find that hydrazine is formed in appreciable amounts when ammonia is passed through a silent discharge at high flow rates. They have not apparently taken into account the fact that hydrazine acts like ammonia when a mixture of these two is passed into sulfuric acid, neutralizing a part of the acid. Hence, the amounts of ammonia decomposition, calculated from their titrations, must be increased by an amount equal to the hydrazine formed. Using these corrected values, it is found that the number of moles of hydrazine formed per mole of ammonia decomposed does not exceed 0.30 even at the highest flow rate used. At nearly constant current strength, the amount of ammonia decomposed per minute was independent of the flow rate and the amount of hydrazine formed per minute varied only four-fold, even when the flow rate varied six hundred times. If one disregards the reactions due to the ions present in the discharge and substitutes current strength for light intensity, then these facts are in accord with the mechanism of Wiig and Kistiakowsky

¹⁴ Bredig, Koenig and Wagner, *Z. physik. Chem.*, **A139**, 211 (1928).

¹⁵ Koenig and Wagner, *ibid.*, **A144**, 213 (1929).

for the photochemical decomposition of ammonia. In the discharge the concentration of hydrazine is ca. 1×10^{-9} mole per cc. ~ 0.02 mm.

The collision yield has been calculated for the reaction¹⁶



The average hydrogen atom concentration in the experiments was 0.06 mm., the ammonia pressure 0.06 mm., and the collision radius 3×10^{-8} cm. Since the reaction tube was 3.5 cm. in diameter and assuming a length for the reaction space of only 10 cm., the number of collisions was 0.44 mole per second. The largest amount of decomposition was about 3.5×10^{-7} mole per second, hence the collision yield was 8×10^{-7} and the corresponding activation energy 8.5 kg. cal. per mole. As pointed out above, the observed decomposition was an upper limit, so this activation energy is a lower limit. Correspondingly, the reverse of Reaction (5) possesses an activation energy > 18.5 kg. cal. per mole. Since the experiments yielded an upper limit for the amount of dissociation, which was small, rather than a true value, it is hardly justifiable to extend these calculations.

Summary

The reactions between hydrogen atoms and hydrazine or ammonia have been studied at low pressure by a flowing method. The concentrations of the atomic hydrogen were measured calorimetrically.

Approximately one mole of ammonia and one mole of permanent gas are produced in the decomposition of one mole of hydrazine by hydrogen atoms. The over-all temperature coefficient of the reactions involved is zero. The qualitative effects of the total pressure, concentration of atomic hydrogen and the concentration of hydrazine were determined. The fluorescence produced in the reaction is described.

Under the conditions of the experiments, the reaction between hydrogen atoms and ammonia was very small and the lower limit for the activation energy 8.5 kg. cal. per mole.

The mechanisms of these two atom reactions have been discussed, especially in connection with the photochemical and electrical dissociation of ammonia.

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¹⁶ Dixon and Steiner,² give for the NH linkage in NH_3 a value of 96 kg. cal. This leads to a heat of reaction for (5) of 6 kg. cal., but, since the accepted value of the heat of dissociation of nitrogen is probably too high, the NH linkage is weaker and the reaction more exothermic. In connection with the heat of dissociation of N_2 see Mulliken, *Rev. Modern Physics*, 4, 1 (1932), and Tate and Lozier, *Phys. Rev.*, 39, 254 (1932).