THE PHOTOCHEMICAL DECOMPOSITION OF HYDRAZINE

Thesis by

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In partial fulfillment of the requirements

for the degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1930

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OBJECTIVES OF THE RESEARCH

The research to be described in this thesis was undertaken in an effort to improve the technique of photochemical investigations in the far ultraviolet as already carried out by Beckman and Dickinson. The chief improvement in the method consists of the use of a system for the continuous recording of the energy incident upon and absorbed by the reaction mixture.

From the chemical standpoint, the problem is of special interest since hydrazine is the only hydride of nitrogen that has not been subjected to a quantitative quantum yield investigation.

ACKNOWLEDGEMENT

INTRODUCTION

The photochemical decomposition of hydrazine has been studied by Elgin and Taylor[1], who did not however attempt to carry out an absolute determination of the quantum yield.

Indeed, in spite of the importance of the nitrogen-hydrogen compounds, perhaps the only unquestionable determination of a quantum yield has been made in the decomposition of gaseous hydrogen azide by Beckman and Dickinson[2]. A yield of $3.0 \pm .5$ molecules per quantum was found. The quantum efficiency in the decomposition of ammonia has been studied independently by Warburg[3] who found 0.25 molecules per quantum absorbed and by Kuhn[4], who found 0.4 - 0.5 molecules per quantum. Owing to the uncertainties in both determinations the solution of the problem is still far from satisfactory.

The experiments of Elgin and Taylor were performed in a quartz cell using the full radiation from a quartz mercury vapor lamp. They concluded that ammonia, nitrogen and hydrogen were formed and that hydrazine decomposes approximately ten times as fast as ammonia under the same conditions. An actinometric determination of the quantum yield in the mercury sensitized reaction gave thirteen molecules of hydrazine decomposed per quantum of λ 2537 absorbed.

The method of investigation to be described in the following pages depends upon the actual measurement of the quanta absorbed during the course of the reaction and the calculation of the molecules decomposed from the analysis of the decomposition products.

## APPARATUS FOR INVESTIGATING THE PRODUCTS OF DECOMPOSITION

The apparatus originally constructed for the investigation and measurement of the decomposition products was designed to measure both the moles of nitrogen plus hydrogen and the moles of ammonia formed. The microanalytical system so constructed operated in the following manner: Immediately after irradiation of the hydrazine, liquid air was applied to the cell trap in order to condense out everything but the nitrogen and hydrogen. These gases were then passed into a modified McLeod gage by means of a Toepler pump and their PV product obtained. The liquid air was then replaced by ether-carbon dioxide snow mixture, which according to Elgin and Taylor permits all the ammonia to pass into the gas phase and retains the hydrazine. The ammonia was then Toeplerized as before and the number of moles measured in the McLeod gage. From these two readings it is possible by simple stoichiometry to calculate the moles of hydrazine decomposed.

An attempt was made to check the analysis by analyzing the fixed gases as well as the alleged ammonia. To do this, an electrically heated platinum filament was sealed into the McLeod gage so that after the moles of nitrogen plus hydrogen had been measured, pure oxygen was introduced into the gage and the hydrogen burnt to water. After freezing out the water on a side trap, the contraction in volume was measured and the mole fraction of hydrogen calculated. It was also thought possible to prove that the gas non-condensable on ether-carbon dioxide was ammonia by decomposing it thermally on the hot filament, measuring the increase in volume and burning the hydrogen so produced.

After considerable testing, the method had to be abandoned for the following reasons: (1) Ammonia can not be accurately measured in glass apparatus because of the "clean-up" action of ammonia on the walls of the apparatus. (2) Oxygen combines rapidly with mercury in the presence of a red hot filament at low pressures. (3) The thermal decomposition of ammonia on platinum, even if complete at these temperatures and pressures, is uncertain because of "clean-up" and outgassing effects of hydrogen on the hot filament.

Another complication discovered during the course of these experiments was the strong adsorbing action of hydrazine on glass, which made it difficult to be removed by pumping and resulted in the liberation of non-condensable gases from the glass walls.

The analytical system finally adopted was that used by Beckman and Dickinson in their studies on hydrogen azide and is shown in Figure 1.
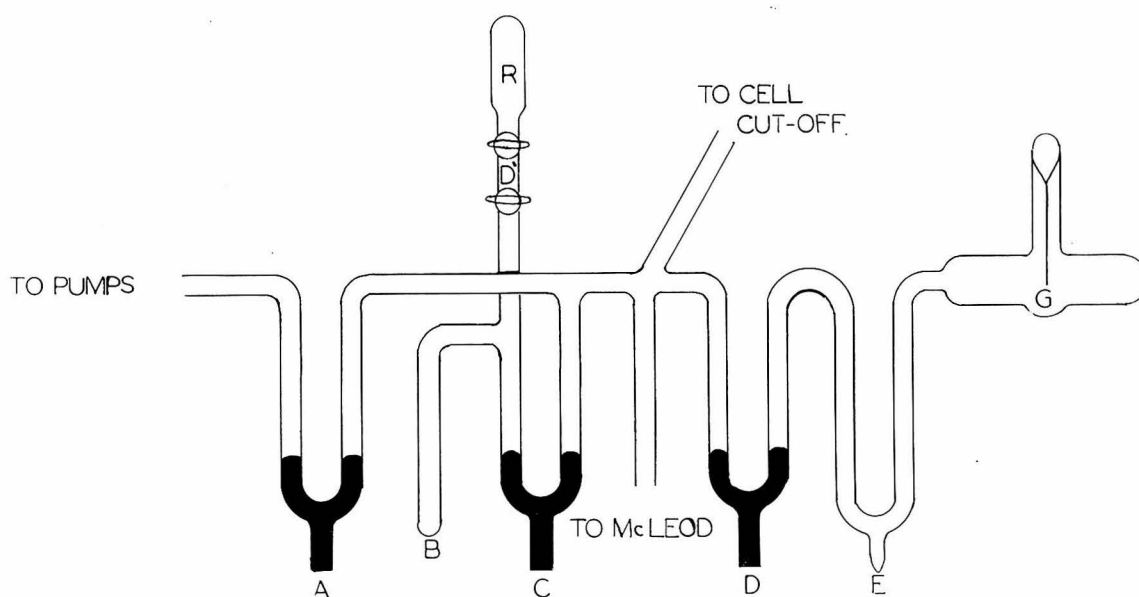
A series of "seal-off" bulbs were also attached to the line during the preliminary experiments in order to make the qualitative tests for ammonia. The method of analysis depends essentially upon the measurement of the $P\sqrt{M}$ of the nitrogen plus hydrogen by means of the quartz fiber gage G and their total pressure by means of the McLeod gage. The use of the quartz fiber gage as a means of analyzing nitrogen-hydrogen mixtures has been fully tested by Beckman and Dickinson[5] and the construction of an efficient form of this device has been described by Beckman[6].

Additional accuracy in the use of the gage has been secured by a special mounting. The gage was held rigidly in a hole bored in a solid brass block, which in turn was clamped rigidly to an upright 2x3 joist. The latter was attached to the vacuum bench at the top and bottom through several layers of hair felt and a loose fitting lag bolt, which served very efficiently to damp out vibrations transmitted to the gage by means of the bench structure.

The use of the quartz fiber gage depends on the fact that the reciprocal of the time for a vibration of the fiber to die down to a certain fraction of its original value is a linear function of the summation of the $P\sqrt{M}$'s for the gases present. Thus, if τ represents the time required for a vibration to die down between two definite marks on the observing telescope scale, then it is a well known fact that the following relation exists:

$$\frac{1}{\tau} = a \sum P_i \sqrt{M_i} + b$$

The gage was calibrated with air at known pressures and from the calibration plot so obtained subsequent "half-lives" were translated

into the corresponding $\sum P_i \sqrt{M_i}$ of the gas present. Since these gases could only consist of nitrogen plus hydrogen, the composition of the mixture was calculated as follows:

$$\sum P_i \sqrt{M_i} = P_{N_2}\sqrt{28} + P_{H_2}\sqrt{2.016}$$

$$\sum P_i \sqrt{M_i} = (1-X_{H_2})\sqrt{28}\, P + X_{H_2}\sqrt{2.016}\, P$$

$$\therefore X_{H_2} = \frac{5.30 - \dfrac{\sum P_i \sqrt{M_i}}{P}}{3.88}$$

The source of radiant energy used was that set up by Beckman and Dickinson for their studies on hydrogen azide. It consisted of a condensed aluminum spark energized by 13,000 volts from the secondary of a transformer whose primary operated at 220 volts and 40 - 60 amperes. The spark was attached directly to the collimator of a Bausch and Lomb quartz monochromator, as shown in Figure 2.
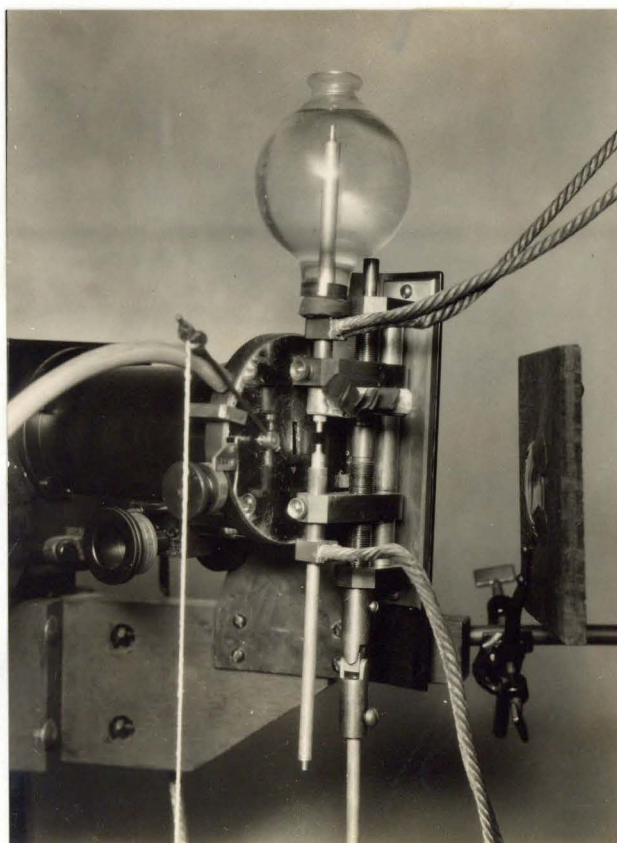
To prevent melting of the electrodes and overheating of the monochromator parts, a stream of compressed air was blown thru the spark in order to direct it away from the monochromator. The quantum yield experiments were carried out using the radiation of λ 1990 exclusively, but the qualitative experiments for the detection of ammonia required the full radiation from an aluminum spark placed 20 cm. in front of the cell.

In the preliminary experiments, hydrazine was introduced from the reservoir R (Figure 1) thru the doser D' into the cell, care being taken to have cut-offs A and D closed and the mercury in the McLeod gage as high as possible. The hydrazine was then condensed in trap B by means of ether-carbon dioxide mixture, cut-off A lowered and ammonia and then other non-condensable gases pumped off. This procedure was repeated three times in order to insure complete removal of gases other than hydrazine. Finally, the hydrazine was allowed to expand into the cell, the cell cut-off raised and the sample illuminated for a definite length of time. After irradiation liquid air was applied to the cell trap, all cut-offs were set on definite marks, and the $\Sigma P \sqrt{M}$ and the total pressure of non-condensable gases measured.

The volume of the system was obtained by trapping a small amount of air in the McLeod gage, measuring its pressure, expanding it into the rest of the evacuated system and again measuring its pressure.

THE PRODUCTS OF PHOTOCHEMICAL DECOMPOSITION

Preparation of Anhydrous Hydrazine.- Anhydrous hydrazine was prepared from the best obtainable Eastman's hydrazine hydrate, by a modification of the method of Hale and Shetterly[7]. The original procedure called for the use of barium monoxide as a dehydrating agent but unfortunately this substance yielded a product lower in hydrazine content than the original hydrate. A test with standard potassium permanganate solution showed a negligible amount of peroxide present in the oxide. After a considerable period of experimentation with barium oxide, it was decided to abandon this substance and distill the hydrazine from fused potassium hydroxide. Three successive distillations from the latter substance at reduced pressure in a current of hydrogen, yielded a product which when analyzed according to the method of Bray and Cuy[8], showed 98.6% hydrazine. This sample was distilled as before directly into a "break-off-easy" bulb containing some pieces of potassium hydroxide, without exposure to the air. This in turn was broken and distilled in vacuo into several smaller "break-off" bulbs by application of liquid air to the proper bulb. After five distillations, the product was assumed to be sufficiently pure without any further analytical tests being made on it.

Preliminary Decompositions.- Previous experiments had shown that hydrazine at room temperatures undergoes a reaction on glass or quartz resulting in the liberation of gases not condensable on liquid air. Since hydrazine has long been known to attack glass when hot, it was assumed that this action was partly due to a purely thermal reaction and partly to adsorption resulting in the displacement of gases not removed from the walls by previous baking of the system. The plausibility of these

assumptions was strengthened by the observation that the outgassing
from the cell after frequent exposures to hydrazine for a week, was
reduced to the small, practically constant amount of 5×10^{-5} mm. in
27 minutes. Some attempts to determine the $P\sqrt{M}$ and hence the composi-
tion of this gas showed it to consist largely of hydrogen. Since this
determination involved readings of τ on the fiber gage of the order of
magnitude of 500-600 seconds, it was not considered a very important de-
termination. The method of correcting the data for outgassing effects
will be resumed under the discussion of the quantum yield experiments.

Preliminary decompositions of hydrazine by λ 1990 at pressures
from 10 - 13 mm. gave non-condensable gases with mol fractions of hydro-
gen around 0.56, which were not considered entirely correct because of
the large uncertain outgassing correction. Two experiments were made in
which the hydrazine at 100 mm. was exposed to the full aluminum spark for
three minutes, in order to produce sufficient ammonia to give a quali-
tative test. This test was made by applying ether-carbon dioxide to the
cell trap after exposure and condensing the ammonia in a seal-off bulb
by means of liquid air. This bulb was then broken under distilled water
and the contents emptied into Nessler's reagent. A reddish-brown colora-
tion indicated the presence of ammonia. No coloration was obtained when the
bulbs were sealed off as before with liquid air on the cell trap to re-
tain the ammonia. Hydrazine produced a grey deposit of mercury with
Nessler's reagent.

The presence of ammonia and a mol fraction of hydrogen around
0.56 seemed to indicate that the decomposition proceeds according to the
reactions,

(a) $2N_2H_4 = 2NH_3 + N_2 + H_2$

(b) $N_2H_4 = N_2 + 2H_2$
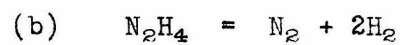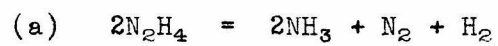
Reaction (a) above would give $X_{H_2} = 0.50$ and reaction (b) would give

$X_{H_2} = 0.66$, whereas the simultaneous reactions would give mol fractions

between 0.50 and 0.66.

APPARATUS FOR DETERMINING QUANTUM YIELDS

Figure 3 is a schematic representation of the apparatus for determining quantum yields.
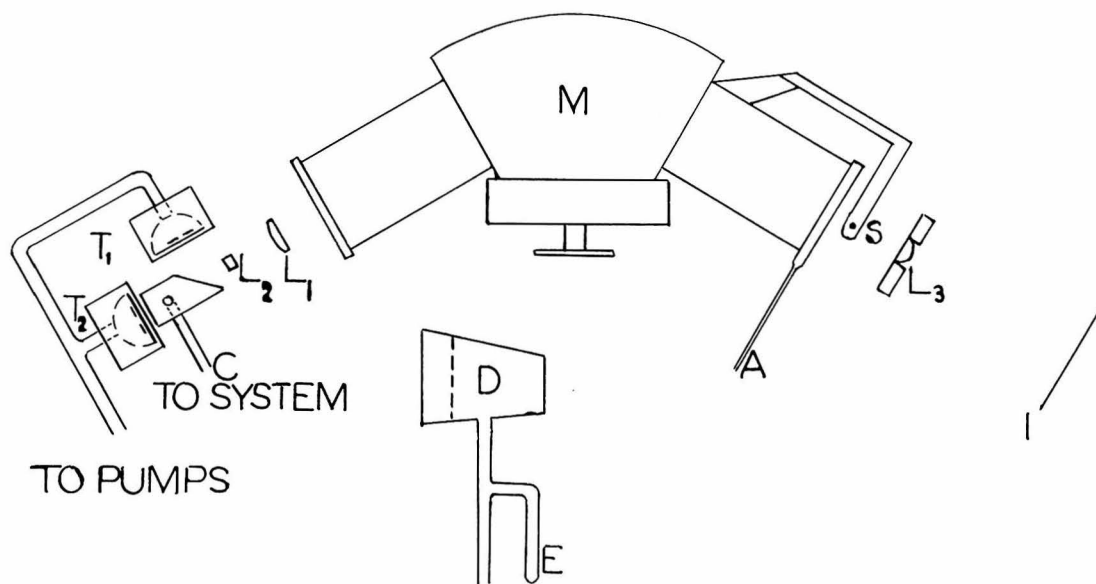
The analytical system was the same as that already described. It was joined thru a cut-off and a quartz pyrex graded seal to the cell C, the whole system being designed to keep the total volume as small as possible. The monochromator, cell and thermocouples were mounted on a table attached to the vacuum bench behind the analytical apparatus. The monochromator and spark set-up have already been described.

The cell was "built-up" of pieces of polished, fused quartz to the shape shown in the diagram. It had a volume of approximately 25 cc. and a mean length of one inch. The front window was built at an angle of 45° to the longitudinal axis of the cell in order to reflect part of the incident radiation on to the thermocouple T_1. Light emerging from the monochromator was brought to a focus on the thermocouples by means of the two 20-diopter, cylindrical, quartz lenses L_1 and L_2. L_1 with axis vertical converges the light in a vertical plane and L_2, with axis horizontal, converges it horizontally, the result being a small rectangular image focussed on T_2. The light reflected onto T_1 was less sharply defined because the images reflected from the front and rear surfaces of the cell window did not quite coincide. Considerable coincidence was gained by properly grinding the front surface of the window.

The two thermocouples were connected to two Leeds and Northrup "High Sensitivity" galvanometers which were set up in conjunction with the automatic recorder shown in Figure 4.

FIGURE 4
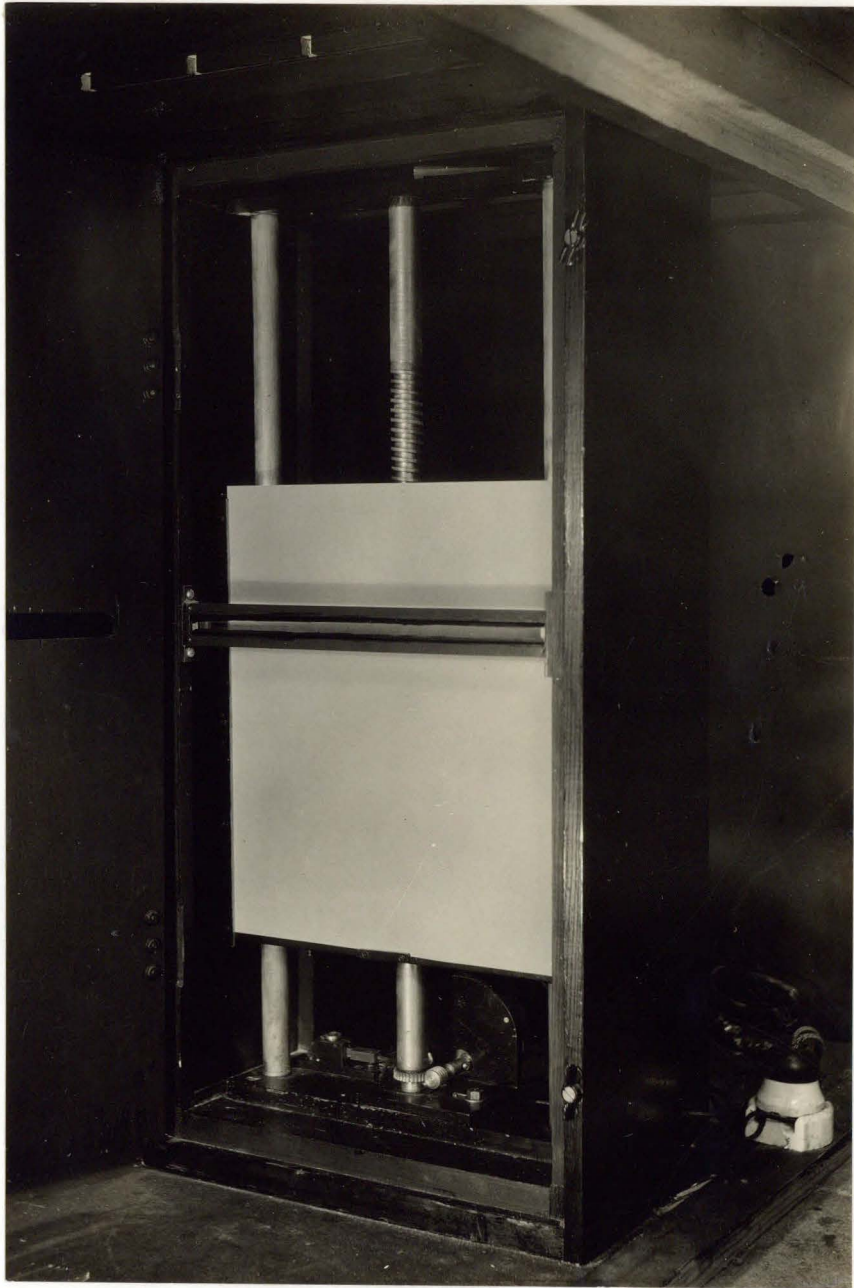
The recorder consisted of a carriage which was made to descend at a uniform rate of speed on an accurately cut screw driven by a Warren Telechron motor. The images from the two galvanometers were brought to a point focus on photographic paper (mounted on the moving carriage) by means of a horizontally placed cylindrical lense. A 200-watt projection lamp mounted in an air-cooled box fitted with a small slit served as light source for the galvanometers. The latter were placed in a carefully shielded wooden box and arranged so as to be free from external vibrations. Complete freedom from electrical disturbances was attained by shielding all electrical parts and connections. The galvanometers were placed at a distance of one meter from the recording paper and the scale tested for linearity. The scale was impressed directly on the photographic paper before developing by exposing the paper for 30 seconds in a RIZEAU to an overhead carbon lamp. This device consists of an ordinary photographic printing frame, the window being a silvered glass accurately ruled in 1/20-inch squares. The whole recording system was contained in a blackened, light-tight compartment underneath one of the laboratory benches. This type of reaction cell and method of energy measurement permitted the continuous recording of the radiation incident upon and absorbed during the course of the photochemical decomposition.

Sensitive vacuum thermocouples of the Coblentz-Petit type were used for measuring the radiant energy. The construction of such a couple is shown in Figure 5.

FIGURE 5
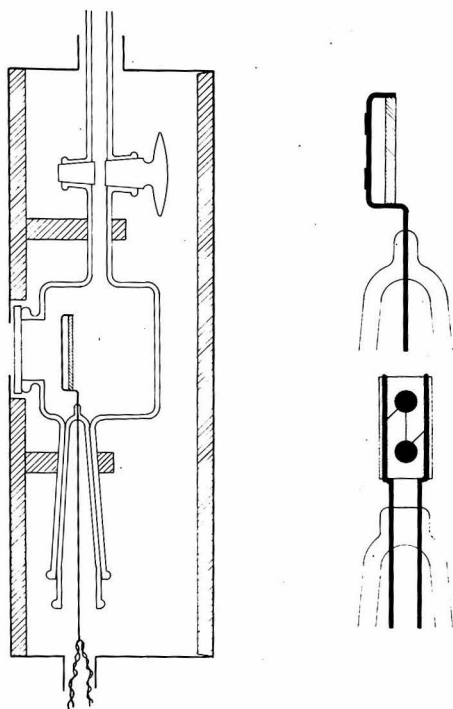
The vanes used in these thermocouples were made of thin aluminum foil, approximately 3.8 x 7 mm. in size. They were blackened with a coating of ordinary commercial dead-black lacquer. The junctions were made of fine bismuth-bismuth (10% tin) wires and were arranged six in series. Three junctions were attached to each vane by means of Du Pont "Household Cement". A piece of fluorescent uranium glass placed behind the vanes was a necessary aid in focussing the light.

The region around the cell and thermocouples was protected from stray light and air currents by means of a cardboard shield and several layers of cotton batting. This was very helpful in preventing shifting of the thermocouple zero.

Calibration of Thermocouples and Cell.- The calibration of thermocouple T_2 was performed according to Bureau of Standards specifications, using two different standard lamps. A brass plate having a hole 0.100 inches in diameter permitted a known amount of the light flux to reach the thermocouple. Since the window of the couple was made of polished fused quartz, it was necessary to determine the transmission of this window or a similar one to the radiation from the standard lamp. This measurement was made by recording the deflections of the couple with and without the plate in the beam of light from the lamp. Two different pieces of quartz gave the following transmissions:

Piece	Transmission
I	0.909
	0.914
II	0.919
	0.918
Mean	0.914

In view of the fact that the maximum deviation of any determination from the mean was less than one percent, it was assumed that the transmission of any thin piece of polished fused quarts may be taken to be 0.914. This was to be expected since the loss of intensity is chiefly a reflection loss for these wave lengths.

In order to translate thermocouple deflections obtained during the course of a run into absolute units it was necessary to measure the transmissions to λ 1990 (at normal incidence) of the rear window of the cell and the window of T_2. This was done by measuring the deflection of T_2 with and without the window in the beam of λ 1990 emerging from the monochromator. A piece of quartz exactly like the window of T_2 was measured instead of the one on the thermocouple. In order to allow for changes in light intensity during these determinations, it was necessary to set up the two couples in the positions shown in Figure 3 and an auxiliary piece of quartz placed at an angle in front of L_2 for the reflection of light onto T_1. The window under investigation was mounted on a metal bracket, as close to T_2 as possible and could readily be swung in and out of the beam of light as desired. In making a transmission determination, the zero reading of the couple was obtained by running the spark and the recorder for two minutes with the vita glass screen in the monochromator closed. The screen was then opened for two minutes and the deflection with the window in the beam recorded. The zero was again taken by closing the shutter for two minutes, during which interval the window was removed from in front of T_2. Again the shutter was opened for two minutes and the full deflection recorded, following which another zero reading was taken. The ratio of the two deflections with the proper correction for

changes in light intensity during the exposures gave the desired transmissions.

Window	Transmission	
Thermocouple window	0.650	
	0.645	
	0.660	
	0.659	
	0.650	
Mean		0.653
Cell window	0.724	
	0.704	
	0.714	
	0.729	
	0.727	
Mean		0.720

After sealing on the rear window of the cell and mounting it rigidly in place, several determinations of the ratio of the deflection of the two thermocouples were made with the cell evacuated. This ratio had to be redetermined whenever the set up was disturbed for any reason. The ratio was obtained for intervals of time corresponding to the actual exposures during a quantum yield determination.

QUANTUM YIELDS

By means of the apparatus just described it was possible to decompose hydrazine photochemically and to measure the quantum efficiency of the reaction. The method of introducing hydrazine into the cell has already been described. Usually, the sample of hydrazine which was to be irradiated was frozen out on the cell trap by means of ether-carbon dioxide mixture and left exposed to the pumps for three quarters, to one hour. During this time the room was completely darkened, all ventilation shut off, and the system allowed to come to temperature equilibrium in order to eliminate shifting thermocouple zero. After standing, the cell cut-off was raised, the ether-carbon dioxide removed and the hydrazine allowed to expand into the cell. Sufficient time was allowed for the hydrazine to vaporize before starting the spark.

With the vita glass shutter closed, the spark was run for one and a half minutes in order to record the thermocouple zero. The shutter was then opened to expose the hydrazine for a definite time and the zero again taken at the conclusion of the exposure. The recording paper was immediately exposed in the Rizeau and developed in the still darkened room. When dry, the deflections were cut out and the mean deflection for the run obtained by weighing. The pressure of the hydrazine was then read on the cell cut-off, liquid air applied to the cell trap, and the total time from the removal of the ether-carbon dioxide until the application of liquid air noted. After expansion of the non-condensables into the system, the cell cut-off was raised until communication between the cell and the rest of the system was just broken. This last precaution was taken to avoid errors in the quartz fiber readings due to the outgassing action of hydrazine retained in the cell.

Owing to the liberation of non-condensable gases during the time the hydrazine was in contact with the cell walls, a correction had to be applied before the number of molecules decomposed could be calculated from the analysis. To do this, non-condensable gases were pumped off the sample after reading the gages and the hydrazine was allowed to stand in the cell for the same length of time as the total duration of the experiment, without irradiation. Liquid air was then restored to the cell trap and the pressure of the non-condensable gases liberated measured on the McLeod. This amount was subtracted from the previous pressure reading in order to obtain the pressure of nitrogen plus hydrogen produced by purely photochemical means. The mol fraction of hydrogen, however, was calculated on the assumption that the composition of these non-photochemical gases would not differ very much from the composition of hydrazine and since they were in small amount would not have an appreciable effect in altering the composition of the photochemically produced nitrogen plus hydrogen. This assumption was necessary inasmuch as quartz fiber gage readings around ten minutes were of doubtful significance, hence the composition of the liberated gases could not be determined accurately.

From these data the number of molecules of hydrazine decomposed may be calculated by simple stoichiometry with no assumptions as to the mechanism of the reaction.

Let a = moles of ammonia produced

b = moles of nitrogen plus hydrogen produced

x = mole fraction of hydrogen

Since the nitrogen and hydrogen in all the products proceeds only from the decomposition of hydrazine, the total number of hydrogen atoms must

equal twice the nitrogen atoms and the moles of hydrazine decomposed
equal one half the total number of nitrogen atoms.

$$\frac{3\,a + 2\,b\,x}{a + 2b(1-x)} = 2$$

(1) $\qquad\qquad a = b(4 - 6x)$

(2) Moles $N_2H_4 = \dfrac{a + 2b(1-x)}{2} = 4b(3/4 - x)$

b was calculated from the perfect gas laws knowing the pressure, volume
and temperature of the nitrogen plus hydrogen.

The number of quanta absorbed were calculated in the following
manner:

Let D_R = mean deflection of thermocouple 1

$\quad D_T$ = mean deflection of thermocouple 2

$\quad R$ = ratio of transmitted to reflected deflections with the cell
evacuated

$\quad T_2$ = transmission of window of couple 2

$\quad T_c$ = transmission of rear window of cell

$\quad k$ = thermocouple sensitivity (ergs per unit deflection)

$\quad E_e$ = energy entering cell per second (ergs)

$\quad E_\iota$ = energy leaving cell per second (ergs)

$\quad t$ = time of exposure

$\quad N_Q$ = total number of quanta of λ1990 absorbed during run

$$E_e = \frac{k\,R\,D_R}{T_2 T_c}$$

$$E = \frac{k\,D_T}{T_2 T_c}$$

Total energy absorbed $= (E_e - E_c)t = \dfrac{k(R\,D_R - D_T)t}{T_2\,T_c}$

$$N_Q = \frac{k(R\,D_R - D_T)t}{T_2\,T_c\,\dfrac{hc}{\lambda}} = \frac{1.013 \times 10^{11}\,k}{T_2\,T_c}(R\,D_R - D_T)t$$

Substituting $T_2 = 0.653$

$\qquad\qquad T_c = 0.720$

$\qquad\qquad k = 1.28$

(3) $\quad N_Q = 2.76 \times 10^{11}(R\,D_R - D_T)t$

In Table I are given the data from which the number of molecules of hydrazine decomposed in each run were calculated. The data for the calculation of the number of quanta absorbed are given in Table II. The quantum yields shown in Table II were obtained by dividing the molecules of hydrazine decomposed by the quanta absorbed.

An inspection of Figure 6 illustrating the variation of the quantum yield with the pressure of hydrazine shows a falling off in the yield as the pressure of the hydrazine decreases. Figure 7 shows an increase in the mole fraction of hydrogen of the non-condensable gases as the pressure of hydrazine decreases. With the exception of Runs 15, 18 and 23 the results show a quite consistent dependence on the pressure of the hydrazine. The results of Run 18 are more liable to error than the others, because of the low light absorption and consequent small quantity of products available for analysis. The utmost accuracy is necessary in the determination of X, since the number of molecules of hydrazine as calculated by Equation 1 is extremely sensitive to errors in this quantity.

TABLE   I

Run	$P_{N_2H_4}$ mm.	Temp. A°	$P_{N_2+H_2}$ mmx10^5	P correction mm x 10^5	$P\sqrt{M}$	X_H	Molecules N_2H_4
3	13	300	4.15	6.0	0.0126	0.582	12.22 x 10^{15}
4	13	300.5	3.83	5.0	.0164	.582	11.27
5	8.0	299.5	4.06	5.0	.01175	.618	9.39
6	8.0	301	3.91	7.0	.0113	.621	8.78
7	11.0	298.5	3.99	5.0	.0119	.598	10.72
8	10.0	298	3.64	5.0	.01072	.608	9.13
9	2.0	299	2.85	6.0	.00808	.634	5.77
10	3.0	299.7	3.47	6.0	.01002	.622	7.76
11	6.0	299	3.63	6.0	.0106	.613	8.73
14	10.5	301.6	3.11	8.0	.00890	.628	6.75
15	6.0	301.5	3.04	8.0	.00852	.644	5.75
16	3.0	302.4	2.59	8.0	.00726	.644	4.85
17	9.8	299.8	2.99	7.0	.00870	.616	7.19
18	2.0	298.3	2.33	8.0	.00667	.629	5.03
19	7.0	298.8	3.22	6.0	.00922	.629	7.05
20	7.0	298.4	3.07	8.0	.00890	.619	7.21
21	12.0	298.3	2.97	5.0	.00867	.613	7.41
22	12.0	298.0	3.00	5.0	.00879	.611	7.57
23	5.0	298.4	2.81	6.0	.00792	.639	5.62
24	5.0	298.3	2.91	6.0	.00827	.634	6.10
25	3.5	298.8	2.68	5.0	.00760	.634	5.61
26	14	298.2	3.06	5.0	.00924	.587	9.05

NOTE: The volume of the system for Runs 3 - 11 was 137.2 cc. and
141.9 cc. for the remaining runs.

TABLE II

| Run	Time exp.	D_R	D_T	R	Quanta entering x 10^{-15}	Quanta leaving x 10^{-15}	Quanta absorbed N_Qx 10^{-15}	Quantum yield Y
3	900	9.58	0.555	3.15	7.50	0.14	7.35	1.66
4	900	9.48	0.928	3.15	7.43	0.23	7.20	1.57
5	900	11.40	1.68	3.15	8.92	0.42	8.50	1.10
6	900	9.87	1.13	3.15	7.72	0.28	7.44	1.18
7	870	11.49	0.89	3.15	8.70	0.21	8.49	1.26
8	900	9.37	1.12	3.15	7.33	0.28	7.05	1.29
9	900	10.92	8.99	3.15	8.54	2.23	6.31	0.915
10	900	10.83	4.26	3.15	8.47	1.06	7.41	1.05
11	900	11.07	1.67	3.15	8.66	0.41	8.25	1.06
14	780	8.54	0.39	2.86	5.25	0.08	5.17	1.30
15	780	10.82	1.74	2.86	6.65	0.37	6.28	0.915*
16	780	9.17	5.57	2.86	5.63	1.20	4.43	1.09
17	787	9.58	0.74	2.86	5.95	0.16	5.79	1.24
18	780	10.03	9.95	2.86	6.16	2.14	4.02	1.25*
19	780	11.13	1.55	2.86	6.84	0.33	6.51	1.08
20	780	10.42	1.46	2.86	6.40	0.31	6.09	1.18
21	780	9.31	0.00	2.86	5.73	0.00	5.73	1.29
22	780	9.64	0.00	2.86	5.93	0.00	5.93	1.28
23	780	10.22	1.90	2.86	6.28	0.41	5.87	0.958*
24	780	9.81	2.24	2.86	6.03	0.48	5.55	1.10
25	780	9.93	4.55	2.86	6.11	0.98	5.13	1.09
26	780	9.38	0.00	2.86	5.77	0.00	5.77	1.57
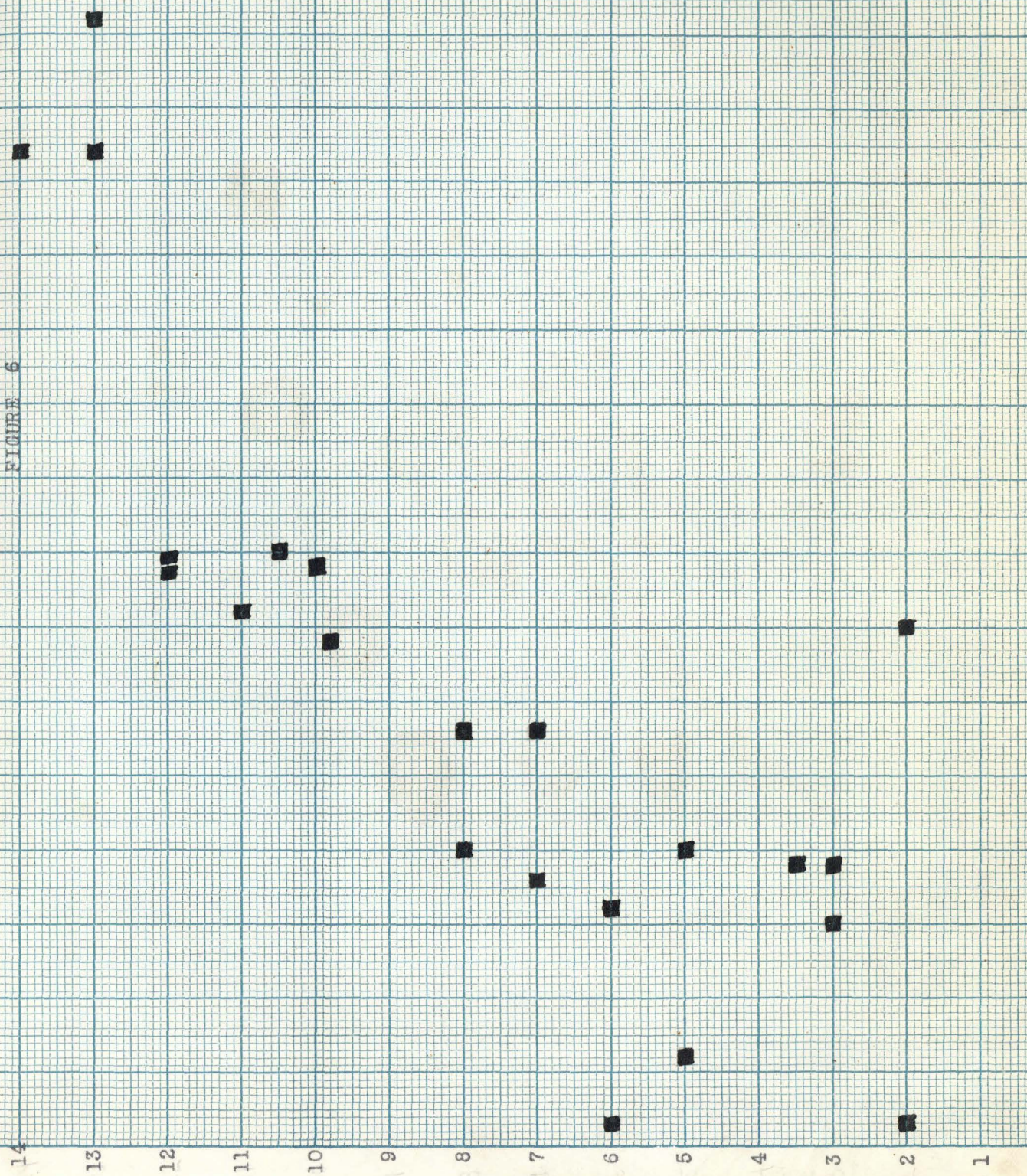
FIGURE 6

FIGURE 7
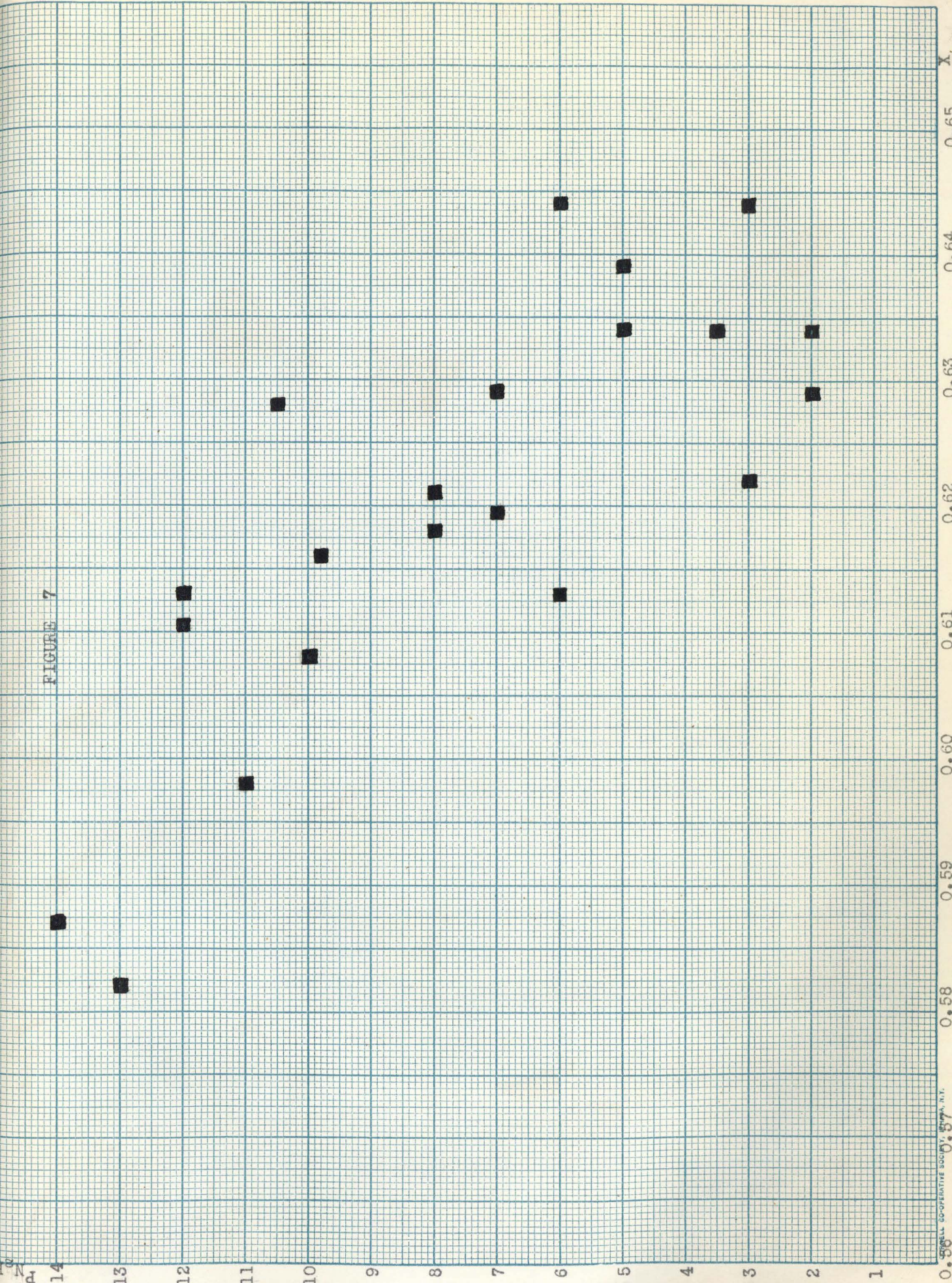
DISCUSSION OF RESULTS

The results of this investigation are in agreement with the results of Elgin and Taylor insofar as the products of the decomposition have been identified as ammonia, nitrogen and hydrogen. These investigators presented data which showed that at the initial stage of the decomposition, the mole fractions of hydrogen and nitrogen in the gases which are non-condensable at liquid air temperatures are equal, i.e., each equal to 0.5, but as the decomposition proceeds the mole fraction of hydrogen increases toward the ultimate value of 0.66 at complete decomposition. These results were taken as evidence that the decomposition of hydrazine proceeded according to the stoichiometric equation

$$2 \ N_2H_4 \ = \ 2 \ NH_3 \ + \ N_2 \ + \ H_2$$
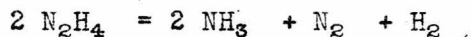
followed by the subsequent decomposition of the ammonia

$$2 \ NH_3 \ = \ N_2 \ + \ 3 \ H_2$$
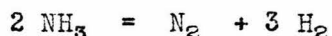
The results of the present investigation are in disagreement with the above, for the observed mole fractions of hydrogen never fell below 0.58, even though less than a tenth of one percent of the hydrazine was decomposed during the run. In the data reported by Elgin and Taylor the minimum decomposition of hydrazine was about thirty percent, for which a mole fraction of hydrogen of 0.52 was obtained. An analysis of the data shows, however, that they are rather inaccurate and are not necessarily in disagreement with the present results. As was stated previously (Equation 1) a stoichiometric relation exists between the amount of ammonia, the amount of non-condensable gas and the mole fraction of hydrogen in the latter gas. If the gases are measured in a system of the same volume and at the same temperature, Equation 1 may be written

$$(4) \qquad P_{NH_3} \ = \ P_{H_2+N_2}(4 - 6X)$$

The data presented by Elgin and Taylor are given in Table III.

TABLE III

Exp't	P_{total} mm.	P_{NH_3}	$P_{H_2+N_2}$ (calc)	X	4 - 6X	P_{NH_3} (calc)
37	6.1	2.2	3.9	0.52	0.88	3.43
35	12.2	3.8	8.4	.50	1.00	8.4
38	13.4	4.2	9.2	.56	0.64	5.8
36	16.2	5.1	11.1	.55	.70	7.77
39	24.1	1.8	22.3	.60	.40	8.92
28	26.5	<0.5	26.0-26.5	.65	.10	72.6

The pressures of non-condensable gases were obtained by subtracting the pressure of ammonia from the total pressure of the products. From Equation 4 were obtained the calculated pressures of ammonia for comparison with the observed pressures. A rather large disagreement is observable. For the present discussion, however, it is more suitable to calculate from Equation 4 the mole fractions of hydrogen which correspond to the observed pressures. These calculated mole fractions are given in Table IV.

TABLE IV

Exp't	$X_{(obs)}$	X_{calc}
37	0.52	0.57
35	.50	.59
38	.56	.59
36	.55	.59
39	.60	.65
28	.65	.66

It will be seen that the calculated values are much more nearly in agreement with the present results. The authors state that their method of analysis was somewhat unsatisfactory as it involved long periods of time (five to six hours) for the diffusion of the gases into the copper oxide combustion region. The fact may also be mentioned that in the previous work the runs lasted as long as three hours. It would appear that the trouble caused in the present work by wall effects would be even more pronounced in the case of such long runs.

MECHANISM OF THE DECOMPOSITION

In the work of Elgin and Taylor both the purely photochemical and the mercury photosensitized decompositions of hydrazine were investigated but the quantum yield determination was attempted in the latter case only. A quantum yield of thirteen was obtained, which was independent of the presence of added nitrogen, hydrogen or ammonia. The inability of nitrogen and ammonia to lower the quantum yield is easily explained since both substances are known to be quite inefficient in quenching the fluorescence of excited mercury atoms.[9,10] The fact that hydrogen did not lower the quantum yield is not so easy to explain, for hydrogen molecules are known to be practically 100 percent efficient in deactivating excited mercury atoms.[9,10] To explain their results, Elgin and Taylor found it necessary to assume a chain mechanism for the sensitized reaction in which such intermediate products as H, N_2H_3 and NH_2 were postulated. They stated further "there is no reason to believe that the purely photochemical decomposition proceeds by another mechanism".

There seems to be no reason for this latter statement and, in fact, the results of the present investigation indicate that this statement is definitely incorrect. It is difficult to see why the "same mechanism" should give a quantum yield of somewhat greater than unity for the purely photochemical decomposition and a yield of thirteen for the photosensitized decomposition.

The results of the present investigation can be plausibly explained on the basis of a rather simple mechanism without the intervention of such remarkable species as N_2H_3, etc. From the work of Elgin and Taylor the absorption spectrum of hydrazine appears to be of the

"predissociation" type. The primary act may therefore be represented by the following reaction:

1. $N_2H_4 + h\nu = N_2H_4'$
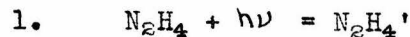
where N_2H_4' represents an activated hydrazine molecule in its predissociated state. This activated molecule may then react in one of three ways, viz:

2a. $N_2H_4' + N_2H_4 = 2NH_3 + N_2 + H_2$

2b. $N_2H_4' = N_2 + 2H_2$

2c. $N_2H_4' = N_2H_4 + h\nu$
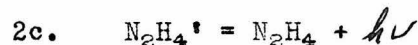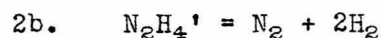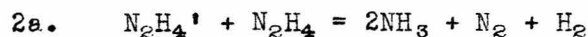
Reaction 2a obviously leads to a quantum yield of 2 and a value of X = 0.5. Reaction 2b leads to a quantum yield of unity and a value of X = 0.67. Reaction 2c leads to a quantum yield of zero. So far as is known, fluorescence has never been observed in the case of predissociated molecules, as is postulated by Reaction 2c, however there is no apparent theoretical reason why fluorescence should not occur.

If it is assumed that the activated hydrazine molecule can react only by 2a and 2b, then the following relation exists between the quantum yield Y and the mole fraction of hydrogen in the non-condensable products

(4) $Y = \dfrac{3 - 4X}{1 - X}$

In Table V are given the calculated values of Y for comparison with the experimental values. It will be seen that at the higher hydrazine pressure, the observed and calculated values of Y agree within the experimental error but at lower pressures, the observed values for the quantum yields are lower than those calculated by Equation 4. This is to be expected if Reaction 2c occurs, since its effect would become increasingly important at the lower pressures.

TABLE V

Run	$P_{N_2H_4}$	X	Y_{exp}	Y_{theor}
26	14.0	0.587	1.57	1.58
3	13.0	.582	1.66	1.60
4	13.0	.582	1.57	1.60
21	12.0	.613	1.29	1.42
22	12.0	.611	1.28	1.44
7	11.0	.598	1.26	1.52
14	10.5	.628	1.30	1.32
8	10.0	.608	1.29	1.45
17	9.8	.616	1.24	1.41
5	8	.618	1.10	1.39
6	8	.621	1.18	1.37
19	7.0	.629	1.08	1.29
20	7.0	.619	1.18	1.37
11	6.0	.613	1.06	1.42
15	6.0	.644	0.915	1.18
23	5.0	.639	0.958	1.22
24	5.0	.634	1.10	1.26
25	3.5	.634	1.09	1.26
10	3.0	.622	1.05	1.35
16	3.0	.644	1.09	1.18
18	2.0	.629	1.25	1.29
9	2.0	.634	0.915	1.26

It would seem therefore, that the above mechanism although not necessarily the only one, offers at least a simple, reasonable explanation of the experimental facts.

SUMMARY

The decomposition of gaseous hydrazine by monochromatic radiation has been investigated over a range of pressures from two to fourteen milli-meters of mercury. Hydrazine appears to decompose simultaneously into ammonia, nitrogen and hydrogen. The results clearly indicate that the composition of the decomposition products and the quantum yield depend on the hydrazine pressure. In this range of pressures, the quantum yield varies between the approximate limits of 1.00 and 1.60. A simple mechanism for the decomposition based on these experimental results has been offered. The photochemical studies of Elgin and Taylor on hydrazine have been criticised in the light of the present results.

BIBLIOGRAPHY

1. Elgin and Taylor, J.Am.Chem.Soc., 51, 2059 (1929).

2. Beckman and Dickinson, J.Am.Chem.Soc., 52, 124 (1930).

3. Warburg, Sitz.Ber.Preuss.Akad., 746 (1911); 216 (1912).

4. Kuhn, J.d.Chem.Phys., 23, 521 (1926).

5. Beckman and Dickinson, J.Am.Chem.Soc., 50, 1870 (1928).

6. Beckman, J.Opt.Soc., 16, 276 (1928).

7. Hale and Shetterly, J.Am.Chem.Soc., 33, 1071 (1911).

8. Bray and Cuy, J.Am.Chem.Soc., 46, 860 (1924).

9. Stuart, Z.Physik, 32, 262 (1925).

10. Mitchell and Dickinson, J.Am.Chem.Soc., 49, 1478 (1927).