

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE THERMAL DECOMPOSITION OF HYDRAZINE

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RECEIVED NOVEMBER 8, 1929

PUBLISHED MARCH 6, 1930

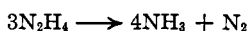
From some experiments performed during an investigation of the photochemical decomposition of hydrazine¹ it appeared that the thermal decomposition in a silica bulb followed a different course from that which resulted from illumination or after activation by excited mercury. With light or excited mercury as a source of activation the hydrazine decomposed to ammonia, nitrogen and hydrogen, according to the equation



but from observations of reaction end-points it appeared to decompose thermally to ammonia and nitrogen



The experiments described below were undertaken as a more extensive study of the nature of the thermal reaction on quartz, and they were compared with a few experiments on the decomposition on heated platinum and tungsten wires. The general conclusions reached were: (1) the decomposition in a silica vessel is heterogeneous, and while it appears primarily to follow the course



kinetically it is of the first order with respect to hydrazine.

(2) The reaction on heated platinum and tungsten wires follows the course



and is of the first order with respect to hydrazine. Hydrogen has a marked retarding effect on the reaction on platinum but practically none in the case of tungsten.

Experimental Method and Discussion of Results

(1) **Decomposition of Hydrazine in a Silica Bulb.**—The course of the reaction was followed by observing the increase of pressure accompanying decomposition and subsequently analyzing the products. Hydrazine is a comparatively high boiling liquid, and if stopcocks are used in the apparatus it is impossible to obtain a reasonable pressure of the substance without condensation at some point. This difficulty was overcome by using in place of stopcocks a form of mercury valve. Two pieces of glass rod had one end ground to fit into correspondingly ground joints in the upper part of a U-bend. Ordinarily, these glass rods rested loosely in the U-bend and there was free communication throughout; but by rais-

¹ Elgin and Taylor, *THIS JOURNAL*, 51, 2059 (1929).

ing a mercury leveling bulb the rods were pushed into position by the mercury and formed a gas-tight stop. It was subsequently found advantageous to make the movable part of the joint of tubing filled with iron filings, so that the stop could be broken against a back gas pressure by means of an electromagnet. The whole internal system was kept at about 100° by means of small furnaces and nichrome wire windings. Hydrazine was purified by distilling from barium oxide several times in vacuo, and a small bulb of it was sealed onto the apparatus. The required pressure was obtained by heating the bulb, and the course of the decomposition followed on a constant volume manometer.

The observed order of reaction obtained both from the effect of the initial pressure upon the time of half change, and from the ratio of the times for 50, 75 and 87.5% decomposition in a particular reaction, is approximately equal to one. This is illustrated by the following table.

T, °C.	Initial pressure, mm.	Time for x % decomposition, seconds		
		50	75	87.5
285	153	2940
298	154	728	1650	3120
298	95.8	639	1275	..
298	78	960	2040	3300
298	24	720
310	111	384
310	52	390	840	..
298 ^a	109	80
298 ^a	50	128	260	..

^a Bulb two-thirds filled with silica.

The figures quoted for the reaction bulb two-thirds filled with silica indicate the heterogeneous nature of the reaction, the reaction rate being increased nearly ten times.

In the next table the final increase of pressure, that is, the "end-point" pressure, is given for a number of reactions. If the decomposition was



the increase of pressure would be 66.6% of the initial pressure; while if it was



it would be a 100% increase of pressure.

Temperature, °C.	271	276	298	298	298	298	298	298	310	298 ^a
Init. press., mm.	30	120	154	98.5	85	78	24	21.8	52	50
Tot. press. incr., mm.	17.5	90	102	61	50	52	17	13	31	31.8
% press. increase	58	74	66	62	59	67	71	60	60	64

^a With silica packing.

These figures show that $3\text{N}_2\text{H}_4 \longrightarrow 4\text{NH}_3 + \text{N}_2$ represents the course of the reaction; this was confirmed by analysis of the products.

Analysis.—A portion of the gaseous products was withdrawn into a gas holder and its pressure measured when occupying a certain volume. It was then circulated (1) through a tube cooled in solid carbon dioxide and ether, (2) through a tube cooled in liquid air, and the diminution of pressure after each operation was noted. The former gave the amount of residual hydrazine, if any, and the latter the amount of ammonia. The residual gas was circulated through a tube of cupric oxide heated to 300° when the hydrogen was burned to water. This was condensed by carbon dioxide and ether, and the diminution of pressure gave the amount of hydrogen. The residue was assumed to be nitrogen.

Temp., °C.	Init. press., mm.	Press. incr., mm.	Products, mm.	Residual N ₂ H ₄ , mm.	NH ₃ , mm.	H ₂ , mm.	N ₂ , mm.
271	30	17.5	29	2	17	2.5	7
298	44.5	25	47	6	26	2.5	10

In each analysis a small amount of hydrogen was found, indicating that part of the reaction is going $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$, but it is insufficient noticeably to affect the end-point pressures.

(2) **Decomposition of Hydrazine on a Heated Platinum Wire.**—The reaction vessel was spherical with a capacity of about 150 cc., and had a platinum filament with tungsten leads through the glass. Electrical energy was supplied by two storage batteries, and was measured by an ammeter and voltmeter and controlled by finely adjustable resistances. Since the thermal conductivity of the gas changed during the course of an experiment, it was necessary continuously to adjust the resistances, so that the ratio of the voltage to the amperage, and hence the resistance of the wire, remained the same. This insured a constant temperature. The temperature-resistance curve of a piece of the same platinum wire was obtained by measurements in a furnace, the temperature of which was known by means of a calibrated thermocouple. Hence the temperature of the filament could be determined, a 5% correction being made for loss of heat by the heavier tungsten leads. Pressures were read on a constant column mercury manometer and the reaction vessel was kept in a water-bath at 25°.

Hydrogen has a strong retarding influence on the decomposition of the hydrazine. This appears both from the rapid initial reaction followed by a falling off in the rate as the products accumulate, and from the inhibition of the reaction when hydrogen is added beforehand. The first point is shown by the following experiment.

INITIAL PRESSURE OF HYDRAZINE, 11 MM.; TEMPERATURE, 205°

Time, minutes	1	2	5	10	15	20	30	40	70	110
Pressure increase, mm.	3	4	5.5	6.7	8	9.6	10.4	11	11.8	12

Nitrogen has considerably less effect than hydrogen in slowing down

the reaction. The following comparative reactions with hydrogen and nitrogen illustrate this point.

Temp., °C.	N ₂ H ₄	Initial press., mm.		Time for x % decomposition, minutes			
		H ₂	N ₂	10	20	50	75
205	11	1	5	13
205	7.5	5.5	...	89	...	255	..
205	8	...	13.5	..	1.5	12	30

In another experiment a mixture of 11 mm. of hydrazine and 12 mm. of hydrogen which decomposed extremely slowly at 205°, when heated to 500° decomposed completely in forty minutes.

The effect is very similar to that found for the thermal decomposition of ammonia by Hinshelwood and Burk.²

The course of the reaction follows the equation



as shown by observations of the end-points of the reaction, and by analysis of the products as described above. As we are dealing here with smaller pressures of gas, the results are less accurate than could be desired, but are sufficient to confirm the nature of the reaction.

Temperature, °C.	173	267.5	205	375	450	530	205
Init. press. N ₂ H ₄ , mm.	8.2	8	11	7	10	11 (H ₂ , 12)	8 (N ₂ , 13.5)
Final press. incr., %	96	90	109	105	110	112	125

RESULTS OF ANALYSES

Temp., °C.	Total products, mm.	N ₂ H ₄ , mm.	NH ₃ , mm.	H ₂ , mm.	N ₂ , mm.
260	16.7	0	8.7
205	15	0.4	6.4	3.4	4.8
267.5	15.2	1.2	7.8	2.0	4.2
205	23	0	13	4	6

(3) **The Decomposition of Hydrazine on a Tungsten Wire.**—The experimental method was the same as for the reaction on platinum. The reaction is not retarded by the presence of excess hydrogen as in the case of the reaction on a platinum filament. On the contrary, it was even accelerated somewhat, but this might have been due to errors in controlling the temperature.

Temp., °C.	Init. press., mm.		Time for x % decomposition, minutes				
	N ₂ H ₄	H ₂	10	20	40	50	75
380	9	..	2	5	16	26	65
360	8	8	1.5	4	10	13	27.5
380	7	14	1	2	6	10	..

Considering the course of an individual decomposition, it would appear to be approximately of the first order. The hydrazine decomposes to ammonia, nitrogen and hydrogen, as on platinum. This is illustrated by the following experimental end-points.

² Hinshelwood and Burk, *J. Chem. Soc.*, 127, 1105 (1925).

Temperature, °C.	500	450	360	380	380
Init. press. N ₂ H ₄ , mm.	7.5	9.5	8	9	9
Init. press. H ₂ , mm.	8	...	14
Tot. press. incr., %	93	106	98	91	93

The measurement of the temperatures of filaments in the manner described above is not particularly accurate, but it is clear that at temperatures approximately close to each other hydrazine decomposes on tungsten and platinum in a manner quite different from that which it follows on quartz, but similar to that which obtains in the presence of excited mercury and on illumination. For this singular behavior on quartz we can at present offer no explanation. It might be pointed out that the discrepancy between the pressures used in the quartz and filament reactions is of no significance, because Elgin, when he first noticed the reaction on quartz, was using pressures of 8 to 10 mm.

In conclusion, we should like to state that we have been enabled to carry out this work thanks to a Procter Visiting Fellowship at Princeton. We should also like to express our appreciation of the advice and helpful suggestions we have received from Professor Hugh S. Taylor.

Summary

The thermal decomposition of hydrazine on quartz and also on platinum and tungsten wires has been studied. On quartz the reaction follows the course $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2$, while on platinum or tungsten it follows the course $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$.

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THE OXIDATION OF BENZALDEHYDE AND FORMALDEHYDE IN THE GASEOUS PHASE

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RECEIVED NOVEMBER 8, 1929

PUBLISHED MARCH 6, 1930

Recently it has been observed that a number of oxidations in the gaseous phase appear to be chain reactions. This is true of the vapor-phase oxidations of phosphorus,¹ of the homogeneous reaction of hydrogen and oxygen,² of the oxidation of propane and the butanes,³ and of several other reactions. The chief characteristic of such reactions is the suppression of the rate of oxidation when the reaction vessel is packed with material of the same nature as itself, and this inhibiting effect is enhanced when the quartz or glass packing is coated with some inert substance like potassium chloride.

¹ Semenoff, *Z. Physik*, **46**, 109 (1927).

² Hinshelwood, *Proc. Roy. Soc. London*, **118A**, 170 (1928).

³ Pease, *THIS JOURNAL*, **51**, 1839 (1929).