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Behavior of the Hydronitrogens and their Derivatives in Liquid Ammonia. VII. Formation of Hydrazine by Thermal Action of Incandescent Filaments Immersed in Liquid Ammonia[1,2]

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Since 1887, when Curtius[3] succeeded in isolating hydrazine in the form of its inorganic compounds, the possibility of obtaining this substance more or less directly from ammonia has engaged the attention of numerous workers. Although many investigations upon the thermal decomposition of ammonia gas have been conducted, no instance of the formation of hydrazine, even in traces, by distinctively thermal means has yet been recorded, so far as the authors have been able to ascertain. The present research was undertaken with a view to ascertaining whether or not the intermediate products of the thermal decomposition of ammonia might dimerize, or might react *inter se*, or with ammonia, to form hydrazine or other hydronitrogens. The use of liquid ammonia at low temperatures afforded an efficient means for the rapid cooling of these unstable products, and for removing them from the heated zone.[4]

Apparatus and Method

The apparatus used throughout the greater part of the work consisted of a test-tube 37 cm. long and of 4 cm. diameter, provided with an outlet and with a forked glass tube that served to support the wire leads and the heating unit. This consisted of a very fine metallic filament, usually tungsten, the ends of which were attached to heavy platinum terminals (diameter, 0.8 mm.) sealed into the glass tube, and connected with the copper wires inside by means of mercury.

In general, the most satisfactory type of filament used was a piece of tungsten wire about 6 cm. in length and 0.05 mm. in diameter. This was prepared in the form of a coil of about 14 turns by winding it around a core consisting of a "Number 18" copper wire (diameter, 1.2 mm.). After withdrawal of the core, the coil was attached to the platinum terminals, each of which protruded about 3 cm. beyond the seal. Filaments less than 4 cm. in length were not coiled.

Refrigeration was accomplished by means of solid carbon dioxide in ether and alcohol during the condensation of the ammonia and throughout the course of the thermal treatment. In the earlier experiments, the filament was heated with the aid of an ordinary 110-volt, 60-cycle alternating current, with suitable resistance in series with the cell. Since equally good yields were found to be obtainable with direct current, however, this source of energy was employed in most of the experiments, in order to facili-

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(1) For the earlier articles of this series see (a) Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911); (b) Browne and Houlehan, *ibid.*, **33**, 1734; (c) 1742 (1911); (d) *ibid.*, **35**, 649 (1913); (e) Browne and Holmes, *ibid.*, **35**, 672 (1913); (f) Browne, Holmes and King, *ibid.*, **41**, 1769 (1919).

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(3) Curtius, *Ber.*, **20**, 1632 (1887).

(4) Preliminary experiments with arc and spark beneath liquid ammonia yielded small but determinable amounts of hydrazine. The yields, however, were of lower magnitude than those obtained with the aid of the incandescent filament.

tate measurement of the power consumed. The approximate temperature of the filament was determined with the aid of an optical pyrometer.

The procedure adopted in a typical experiment was essentially as follows. Pure anhydrous ammonia gas was condensed until the test-tube was about one-third full of liquid. The volume of liquid in the tube, which had previously been calibrated with water, could at any time be ascertained within 1 cc. by measurement of the distance between the meniscus of the liquid and the top of the tube. In order to minimize the danger of local overheating and resultant breakage of the tungsten filament, the temperature was raised gradually by decreasing the series resistance, until a uniform incandescence was obtained. Thereafter, the temperature was raised rapidly to about 3000°. Throughout the course of the experiment, readings of the voltage drop across the filament and of the amperage were made at frequent intervals. The duration of the thermal treatment was noted, as well as the rate of evolution of the fixed gases. The ratio of nitrogen to hydrogen in the unabsorbable gases was also determined by analysis. The pyrolysis was continued until the level of the liquid had been lowered to within about 1 cm. of the filament. The heating unit was now removed, and the solution was concentrated by spontaneous evaporation of ammonia, to a volume of about 3 cc. In order to prevent possible loss of hydrazine as a result of the liberation of the heat of hydration and neutralization this residual solution was cooled to $-78°$. Ten cc. of water was added drop by drop, with constant shaking, and dilute sulfuric acid was finally introduced in slight excess. Hydrazine was determined by the procedure outlined below.

Detection and Determination of Hydrazine.—Samples of the solution to be tested were found to show strong reducing action toward potassium permanganate, ammoniacal silver, and Fehling's solutions. The distillate obtained from a sample strongly acidified with sulfuric acid gave no evidence of the presence of hydronitric acid when subjected to the usual ferric chloride and silver nitrate tests.[5] When dilute hydrogen peroxide solution was slowly introduced beneath the surface of the boiling solution, however, appreciable amounts of hydronitric acid were obtained in the distillate. The formation of this product under these conditions affords irrefutable evidence of the presence of hydrazine in the solution tested.[6]

In order to isolate the hydrazine formed, samples of the residual solution, after acidification with sulfuric acid, were evaporated to small volume and treated with ethanol at 0°. The resulting crystals, after filtration, were recrystallized four times from small amounts of water slightly acidified with sulfuric acid. Hydrazine was determined in the final product by the potassium bromate method suggested by Kolthoff.[7]

Anal. Subs., 0.0746, 0.0560, 0.0490. Calcd. for $N_2H_4 \cdot H_2SO_4$: N_2H_4, 24.63. Found: N_2H_4, 24.47, 24.62, 24.40.

Experimental Results

Several series of experiments have been performed with a view to ascertaining the influence, upon the yields of hydrazine obtained, of the following factors: (1) nature of the filament, (2) dimensions of the filament, (3) temperature of the filament, (4) temperature of the liquid ammonia, (5) volume of the liquid ammonia, and (6) duration of the thermal treatment.[8] The results of these experiments are presented in Tables I to IV.

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[5] Browne, THIS JOURNAL, **27**, 551 (1905).

[6] Browne, *Science* (N.S.), **21**, 260 (1905); Browne and Shetterly, THIS JOURNAL, **31**, 783 (1909).

[7] Kolthoff, *ibid.*, **46**, 2009 (1924).

[8] The possible influence of various other factors, including (a) pressure, (b) rate of decomposition of hydrazine under prevailing conditions, and (c) presence in the liquid ammonia of certain solutes capable of exerting a catalytic action, or of removing the hydrazine from the zone of decomposition, has not been discussed in the current article, but is under investigation by the authors.

TABLE I

INFLUENCE OF NATURE OF FILAMENT UPON FORMATION OF HYDRAZINE

	Filament							
Expt.	Nature	Diam., mm.	Length, cm.	Approx. temp., °C.	Duration of thermal treatment, min.	Gross power consumption, k. w. h.	Hydrazine formed, mg.	Yield of hydrazine per k. w. h., g.
1	Pt	0.44	1 to 15	Below red heat	..	..	0.00	0.00
2	Pt	.32	6	Below red heat	60	..	.00	.00
3	Pt	.17	1 to 15	Below red heat	..	..	.00	.00
4	Ni-Cr	.65	1 to 6	......	..	..	..	...
5	Ni-Cr	.25	8	Dull red	105	..	Trace	...
6	Mo	.13	4	2400	13	0.023	4.7	.21
7	Thoriated W	.05	6	3000	30	.075	19.3	.26
8	W	.13	4	3000	30	.074	18.0	.24
9	W	.05	3.5	3000	30	.082	31.0	.38
10	W (+Pt)	.05	6	3000	30	.094	32.8	.35

It was not found possible to maintain platinum filaments at red heat beneath the surface of liquid ammonia, owing to the ease with which they "burned out" as the result of local overheating. Filaments of either greater resistivity or higher melting point, or of both, were found better able to withstand the unavoidable thermal variations, and could be held at incandescence for prolonged periods without marked deterioration.

Experiment 10 was performed in order to ascertain whether or not the contacts between incandescent tungsten filament and platinum terminals exerted any catalytic influence upon the formation of hydrazine. Two pieces of platinum wire, each 1 cm. long and of 0.17 mm. diam., were braided into the tungsten coil, so as to make numerous contacts with the coil, although not in contact with each other or with the platinum terminals. The substantial identity of the yields obtained in Experiments 9 and 10 indicates that no such influence is exerted. This is not to be construed, however, as excluding the possibility that the process taking place at the surface of the tungsten filament itself may not be to some extent catalytic in nature.

From the results of the experiments listed in Table I it is obvious that the tungsten filament is the most satisfactory of those employed. In all subsequent experiments, therefore, the tungsten filament exclusively has been used.

In all of the experiments recorded in Table II, the filament was maintained at a temperature above 2600°. The heating unit employed in Experiment 11 consisted of two tungsten wires brought together under liquid ammonia with the original intention of obtaining a small arc. The ends of these wires became fused together almost immediately, however, and remained incandescent, at the point of union only, throughout the experiment. The data obtained in this series of experiments point to the conclusion that the yield of hydrazine is increased by the use of filaments of smaller diameter, and by the use of straight rather than coiled filaments. On the other hand, the yield is apparently not affected by the length of the filament.

TABLE II

INFLUENCE OF DIMENSIONS OF TUNGSTEN FILAMENT UPON FORMATION OF HYDRAZINE

	Filament								
Expt.	Diam., mm.	Length, cm.	Form	Potential drop, volts	Current, amp.	Duration of thermal treatment, min.	Gross power consumption, k. w. h.	Hydrazine formed, mg.	Yield of hydrazine per k. w. h., g.
11	0.9	...	(*Vide infra*)	26	13.1	13	0.074	3.7	0.05
8	.13	4	Straight	18	8.2	30	.074	18.0	.24
12	.05	2	Straight	39	3.7	18	.043	15.3	.35
9	.05	3.5	Straight	51	3.2	30	.082	31.0	.38
13	.05	6	Coiled	49	2.45	17	.034	9.31	.27
14	.05	8	Coiled	48	2.3	288	.530	127.2	.24
15	.05	15	Coiled	78	2.7	36	.126	33.0	.26

TABLE III

INFLUENCE OF TEMPERATURE OF TUNGSTEN FILAMENT UPON FORMATION OF HYDRAZINE

Expt.	Approx. temp., °C.	Potential drop, volts	Current, amp.,	Duration of thermal treatment, min.	Gross power consumption, k. w. h.	Hydrazine formed, mg.	Yield of hydrazine per k. w. h., g.
16	2000	22	2.15	60	0.047	6.28	0.13
17	2200	28	1.90	60	.053	6.03	.11
18	2400	35	1.92	40	.045	5.64	.13
19	2500	41	2.68	30	.055	15.0	.27
20	2700	49	2.3	31	.058	14.9	.26
21	2900	64	3.35	22	.079	21.9	.28
22	3200	83	3.2	19	.084	22.1	.26
23	3400	115	3.2	5.5	.034	9.68	.29

Throughout the experiments described in Table III, filaments duplicating as closely as possible that used in Experiment 13 (Table II) were employed. It is clear from the results obtained that at temperatures of 2500° or higher the yields of hydrazine were about twice as high as those at lower temperatures. This may be in part attributable to the presence of a more nearly continuous film of gas, which served as thermal insulator for the filament at higher temperatures. On the other hand, the higher yields may be due to a change in the inherent mechanism of the pyrolysis at higher temperatures.

The first four experiments recorded in Table IV prove that the yield of hydrazine is independent of the temperature of the liquid ammonia at atmospheric pressure. The relatively great decrease in volume noted in Experiments 13 and 25, resulting both from vaporization and from decomposition of the liquid, is ascribable to the fact that no refrigerant was used. The temperature of the liquid ammonia never rose above −36°, however, even when external heat was applied, owing to a reduction of the partial pressure of the ammonia caused by the escape of gaseous products of the pyrolysis.

The remaining experiments show that the net yield of hydrazine varies inversely with the concentration of hydrazine in solution, for the reason

TABLE IV

INFLUENCE OF VOLUME, DURATION OF TREATMENT, AND TEMPERATURE OF LIQUID AMMONIA UPON FORMATION OF HYDRAZINE

Expt.	Volume of liquid NH_3, cc. Initial	Added	Final	Loss	Temp., °C.	Duration of thermal treatment, min.	Gross power consumption, k. w. h.	Hydrazine formed, mg.	Yield of hydrazine per k. w. h., g.	Final concn. hydrazine in soln., %
13	150	80	55	175	−36 to −38	17	0.034	9.31	0.27	...
24	85	0	72	13	−70 to −78	16	.031	7.39	.24	...
25	120	188	83	225	−36 to −38	33	.063	19.1	.30	...
21	103	0	75	28	−50 to −55	22	.079	21.9	.28	...
20	100	0	35	65	....	31	.058	14.9	.26	0.068
26	100	165	35	230	....	124	.233	59.5	.26	.27
14	210	113	123	200	....	288	.530	127.2	.24	.16
27	15	...	15	...	....	236	.614	90.4	.15	.96
28	150	...	150	...	....	165	.613	154.0	.25	.16

that thermal decomposition of this product increases at higher concentrations. This reverse reaction is therefore influenced by the volume of liquid ammonia, and by the duration of thermal treatment. The effect of volume is more specifically illustrated in Experiments 27 and 28, in which the recorded volume was maintained constant throughout the period of thermal threatment by condensation of additional ammonia to compensate for loss. In No. 27 an apparatus smaller than that previously described was employed. In all of the 28 experiments, with this single exception, the volume of ammonia used was sufficiently large to render the effect of the reverse reaction practically negligible.

Ratio of Hydrazine Formed to Ammonia Decomposed.—Under the conditions prevailing in the experiments described in the preceding paragraphs, it was found that evolution of nitrogen and hydrogen in the ratio of 1:3, as shown by analysis, occurred at the rate of about 400 liters per k. w. h. The best yield of hydrazine obtained amounted to 0.38 g. per k. w. h., or to about 0.25% of the ammonia decomposed.

Proof that Hydrazine Formation is not Due to Photochemical Action.—Experiments were conducted in which a straight tungsten filament 3 cm. long was enclosed in a quartz tube (15 × 2 cm.), which was immersed in liquid ammonia. In each experiment a current of ammonia gas was passed through the quartz tube, and in one case the filament was surrounded with liquid ammonia. No detectable amount of hydrazine was found in the outer tube, although in each case appreciable quantities were formed in the quartz tube.

Spectrograms were taken of the quartz-enclosed filament held at 3200° and immersed either in liquid ammonia or in the vapors above the liquid. These showed a continuous spectrum with no absorption bands, and with range extending to $\lambda = 3400$ Å.

Discussion of Results

In the attempt to account for the formation of hydrazine as a product of the decomposition of ammonia by various means, several hypotheses have been advanced. Raschig,[9] for example, has suggested the initial formation of imino groups, which subsequently condense with ammonia molecules to form hydrazine

$$NH + NH_3 \longrightarrow N_2H_4 \qquad (1)$$

This explanation has seemed reasonable to certain other investigators, including Bredig, Koenig, and co-workers,[10] Hofmann and Korpiun,[11] and Gedye and Allibone.[12]

The liberation of amino groups, on the other hand, which later either dimerize, or react with ammonia to yield hydrazine, is deemed more probable by others, including Kassel and Noyes,[13] and Taylor and co-workers[14]

$$2NH_2 \longrightarrow N_2H_4 \qquad (2)$$
$$NH_2 + NH_3 \longrightarrow N_2H_4 + H \qquad (3)$$

Until further experimental evidence is available, the authors of the present article feel disinclined to express any preference for one of these hypotheses over the other. From the work of Friedrichs[15] in this Laboratory, it seems clear that hydrazine, once formed, would yield no compound with ammonia, even in the liquid state at low temperatures. During the past year another worker in this Laboratory, V. J. Sabetta, has succeeded in obtaining, by purely inorganic reactions, relatively large quantities of a strong reducing agent, proved to be neither hydrazine nor hydroxylamine, and probably to be regarded either as *diazene* (diimide), or as some other polymer of the imino group. Work upon this substance, both in the free state, and in the form of its inorganic compounds and derivatives, is being continued, and will be made the subject of a future communication. From the observation that the new reducing agent in liquid ammonia solution does not react with the solvent to form hydrazine, it is apparent that polymerized imino groups, at least, do not react in accordance with Equation 1.

The two mechanisms expressed in Equations 1 and 3 seem to have been suggested largely as a matter of expediency, in order to avoid the necessity of assuming the direct dimerization of unstable amino groups, collisions of which can occur at best only with relative infrequency. One possibility that seems as yet to have escaped attention is that of the union

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(9) Raschig, *Z. physik. Chem. Unterr.*, **31**, 138 (1918); through *Chem. Soc. J.*, [2] **116**, 148 (1919).

(10) (a) Bredig and Koenig, *Naturwissenschaften*, **16**, 493 (1928). See also German Patent 454,699 to I. G. F., *Chem. Zentr.*, **99**, 2528 (1928); (b) Bredig, Koenig, and Wagner, *Z. physik. Chem.*, **139A**, 211 (1928); (c) Koenig and Wagner, *ibid.*, **144A**, 213 (1929); (d) Koenig and Brings, *ibid.*, Bodenstein Festband, 541 (1931).

(11) Hofmann and Korpiun, *Ber.*, **62B**, 3000 (1929).

(12) Gedye and Allibone, *Proc. Roy. Soc.* (London), **130A**, 346 (1931); *J. Chem. Soc.*, 1158 (1932); Gedye and Rideal, *ibid.*, 1160, 1169 (1932).

(13) Kassel and Noyes, THIS JOURNAL, **49**, 2495 (1927).

(14) Bates and Taylor, *ibid.*, **49**, 2438 (1927); Elgin and Taylor, *ibid.*, **51**, 2059 (1929). See also Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

(15) Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

of amino groups with ammonia by a process of solvation, which might serve to stabilize these intermediate products, permitting ultimate condensation to form hydrazine, with liberation of ammonia

$$NH_2 + NH_3 \longrightarrow NH_2 \cdot NH_3 \qquad (4)$$

$$2NH_2 \cdot NH_3 \longrightarrow N_2H_4 + 2NH_3 \qquad (5)$$

Koenig and Brings[10d] have used a film of liquid ammonia to remove the intermediate products from the discharge tube in their experiments.[16] Whether the formation of intermediate products in the experiments described in the present article be attributed to (1) thermal action, involving rapid rotational, vibrational, or translational motion of the ammonia molecules, or of their constituent atoms, (2) thermionic action, or (3) catalytic action at the surface of the filament,[17] it seems probable that the primary reaction occurs in the layer of gas surrounding the filament. The liquid ammonia, in immediate proximity to this zone of primary action, serves not only to quench the initial products, but also to furnish a favorable medium for secondary reactions such as those expressed in Equations 4 and 5.

From the fact (Table III) that the yields of hydrazine obtained at temperatures between 2500 and 3400° are practically constant, it may be inferred that the intensity of thermionic emission is not an important factor, since this is known to vary directly as the twelfth power of the temperature.

Summary

Hydrazine is formed in appreciable quantities by the action of incandescent metallic filaments (preferably tungsten) in liquid ammonia. The influence of such factors as the nature, dimensions, and temperature of the filament, the temperature and volume of the liquid ammonia, and the duration of the thermal treatment has been investigated. The highest yields, about 0.38 g. N_2H_4 per (gross) k. w. h., were obtained with a straight tungsten filament of 0.05 mm. diameter heated to a temperature of 3000°.

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[16] "An der Innenwand des Rohres scheidet sich bei Kühlung mit Aceton-Kohlensäuregemisch eine dünne Schicht flüssigen Ammoniaks ab, welche das in der angrenzenden Gasschicht durch die Entladung gebildete Amid bzw. Imid aufnimmt und als Hydrazine aus dem Entladungsbereich hinwegschwemmt. "Upon the inner wall of the tube there separates out, on cooling with an acetone-carbon dioxide mixture, a thin layer of liquid ammonia, which absorbs the amide or imide formed in the adjacent gas layer by the discharge, and washes it away, as hydrazine, from the zone of discharge."

[17] Mittasch and Frankenburger [*Z. Elektrochem.*, **35**, 920 (1929)] have noted the formation of an imide, $W_x(NH)$, stable from 250–360°, but decomposing at higher temperatures.