[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Behavior of the Hydronitrogens and their Derivatives in Liquid Ammonia. VIII. Influence of Pressure upon Yields of Hydrazine Obtained by Pyrolysis of Liquid Ammonia[1,2]

BY D. H. HOWARD, JR., AND A. W. BROWNE

The influence of various factors upon the formation of hydrazine as a product of the thermal action of incandescent filaments immersed in pure liquid ammonia at atmospheric pressure has already been investigated.[1] In the current article is described the effect of two additional factors: (1) variation in pressure from 80 to 1870 mm., and (2) presence of certain inorganic or organic solutes in the liquid ammonia.

Apparatus and Method

An improved apparatus (Fig. 1) of the type described in an earlier article[1] was employed. Throughout all of the experiments the tungsten filament was heated to at least 3000° by means of the direct current. For the work at varying pressures a filament about 1 cm. in length and 0.05 mm. in diameter was used. Reduced pressures were maintained constant to within ±3 mm. with the aid of two large Chapman pumps. For pressures above atmospheric the evolved gases were allowed to escape through a column of mercury of the desired height. For the experiments, all at atmospheric pressure, upon the effect of solutes, a filament about 3.5 cm. in length and 0.05 mm. in diameter was used. A control test was performed with each solute to ascertain whether or not it would interfere in the subsequent determination of hydrazine by the bromate method of Kolthoff.[3]

Experimental Results

Influence of Pressure upon Yields of Hydrazine.—The results obtained by the pyrolysis of liquid ammonia under pressures varying from 80 to 1870 mm. are summarized in Table I, and plotted in Fig. 2.

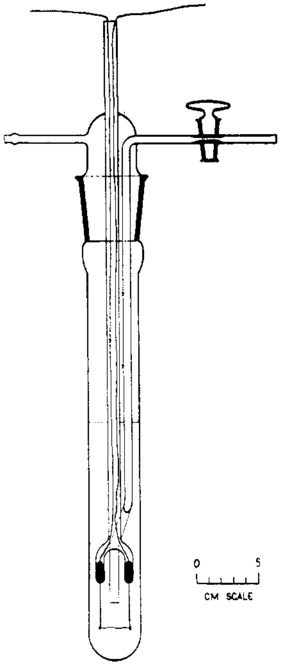

Fig. 1.

These data may be expressed by the empirical equation $x^{0.423}y = 5.2$, which is shown graphically in Fig. 2, and is seen to be in satisfactory accord with the experimental results.

---

(1) For a list of the earlier articles of this series see Howard and Browne, THIS JOURNAL, **55**, 1968 (1933).

(2) The current article is based upon a part of the thesis to be presented to the Faculty of the Graduate School of Cornell University by David H. Howard, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This investigation is an outgrowth and continuation of the work supported by Grant No. 158 from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

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

TABLE I

INFLUENCE OF PRESSURE UPON FORMATION OF HYDRAZINE

Expt.	Press., mm.	Power, k. w. h.	N_2H_4 formed, mg.	R (g. N_2H_4 per k. w. h.)
1	80	0.0220	17.0	0.774
2	100	.0405	29.6	.732
3	110	.0251	17.7	.705
4	125	.0296	17.4	.588
5	150	.0361	20.8	.576
6	155	.0434	25.8	.594
7	200	.0276	14.1	.512
8	250	.0414	21.4	.517
9	300	.0376	18.9	.503
10	350	.0321	14.8	.461
11	400	0.0379	18.3	0.483
12	450	.0253	9.72	.384
13	500	.0364	11.3	.312
14	550	.0314	12.3	.392
15	600	.0352	12.3	.349
16	740	.0424	15.0	.353
17	1100	.0552	14.8	.268
18	1480	.0672	16.0	.238
19	1870	.0600	12.3	.205

A possible explanation of the inverse variation of hydrazine yield with pressure lies in the greater rapidity with which the free radicals or other intermediate products, or even the hydrazine itself, are withdrawn at lower pressures from the heated zone.

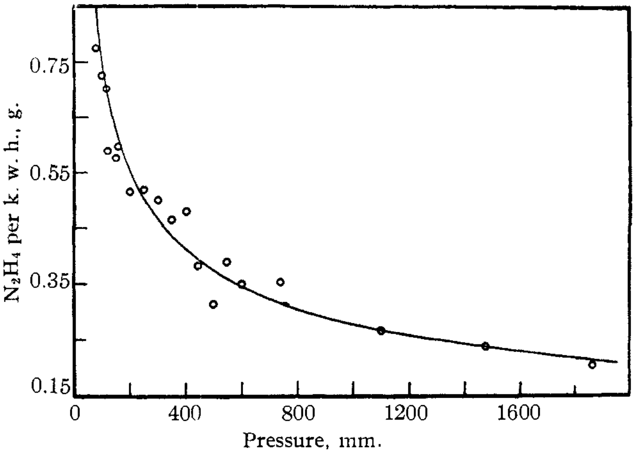

Fig. 2.

Influence of Solutes upon Yields of Hydrazine.—Each of the solutes under investigation was dissolved in the liquid ammonia before the thermal treatment was initiated. The results obtained are recorded in Table II.

Experiment 20 served as a control under the prevailing conditions. The solutes chosen comprise substances which exhibit in liquid ammonia the typical properties of an acid, base, salt or neutral organic compound. Electrolysis was found to occur to an appreciable extent whenever the conductance of the solution was relatively high. In this event part of the current passes between the platinum terminals of the heating unit through

TABLE II

INFLUENCE OF SOLUTES UPON FORMATION OF HYDRAZINE

Expt.	Solute Comp.	Solute g.	Vol. NH_3, cc. Int.	Vol. NH_3, cc. Final	K.w.h.	N_2H_4 formed, mg.	R (g. N_2H_4 per k.w.h.)
20	....	.....	63	34	0.0624	17.9	0.287
21	NH_4Cl	0.0103	70	48	.0510	16.0	.314
22	NH_4Cl	.1377	68	52	.0386	12.7	.328
23	NH_4Cl	1.273	70	56	.0376	6.09	.162
24	K	1.5	65	60	....	...	...
25	KNH_2	Satd. soln.	83	70	.0361	0.2	.005
26	NaCl	Satd. soln.	75	65	.0472	9.01	.191
27	Gelatin	Satd. soln.	75	40	.0400	15	.375
28	Sucrose	10	65	40	.0619	23.8	.384

the solution instead of through the filament, thereby causing an apparent decrease in the yield of hydrazine.[4]

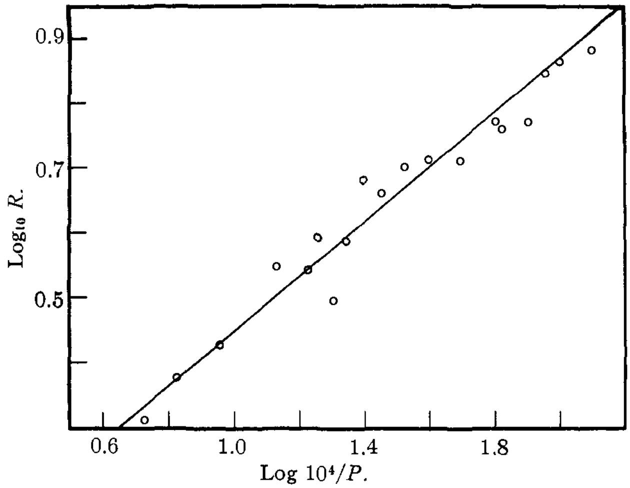

Fig. 3.

In Experiment 24 the filament was repeatedly observed to "blow out" almost immediately, probably as a result of the action of potassium upon tungsten at high temperatures. Small amounts of an oxidizing agent were found in the solution. In Experiment 25 the same difficulty was experienced to a lesser degree, owing to the formation of metallic potassium by electrolysis. The extremely low yield of hydrazine may be attributable to the presence of the oxidizing agent noted in the preceding experiment. The gelatin used in Experiment 27 was found to have a slight reducing action, for which a suitable correction was made in calculating the yield of hydrazine.

---

(4) Very small amounts of a reducing substance, which has not yet been isolated or positively identified, but which is probably hydrazine, have been obtained repeatedly, during control experiments, by electrolysis of a solution of ammonium chloride in liquid ammonia between platinum or graphite terminals. Further work upon the formation of hydrazine by electrolysis of liquid ammonia solutions is in progress.

Summary

The amount of hydrazine formed by pyrolysis of liquid ammonia with the aid of a tungsten filament heated to 3000° was found to vary inversely with the pressure, in accordance with the equation $x^{0.423}y = 5.2$.

The yields of hydrazine under the conditions of the experiments varied from 0.774 g. per k. w. h. at 80 mm. to 0.205 g. at 1870 mm.

The presence of solutes of various types was in no case found to augment the yield of hydrazine beyond the value to be expected from the equation.

ITHACA, N. Y. RECEIVED APRIL 10, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY AND THE UNIVERSITY OF BUFFALO]

The Catalysis of Eder's Reaction by Cobalt Compounds[1]

BY G. H. CARTLEDGE AND T. G. DJANG

The photochemical reduction of mercuric chloride to calomel by oxalates, which is known as Eder's reaction, has been the object of many investigations.[2] No completely satisfactory theory of the reaction mechanism has yet been offered, although it is a chain reaction according to Roseveare and Olson[2] and Oberhauser and Schormüller.[2] The reaction may be induced in the dark by the manganioxalate ion, $Mn(C_2O_4)_3^{3-}$, and by the analogous cobaltic complex, whereas at room temperature the ferrioxalate ion is inactive. It has seemed to us that a comparison of the action of these complexes might well throw light upon the manner in which the inductor participates in the reaction mechanism.

Induction by Potassium Cobaltioxalate

Materials.—The mercuric chloride and potassium oxalate used were Baker C. P. chemicals, which were further recrystallized three times to reduce the iron content.

The potassium cobaltioxalate, $K_3Co(C_2O_4)_3 \cdot 3.5H_2O$, was prepared from cobaltous chloride and potassium oxalate using lead dioxide as the oxidant, following a modification of the method proposed by Jaeger and Thomas.[3] The complex salt can be recrystallized readily in the cold or by the use of alcohol, and is much more stable than the corresponding manganic salt. Crystals kept in the dark at laboratory temperature show no alteration after three years. Determinations of cobalt and oxalate on a sample washed with alcohol and ether and dried over calcium chloride agreed closely with the

---

[1] The larger part of this paper is abstracted from a dissertation presented by T. G. Djang to the Faculty of Philosophy of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Eder, *Ber.*, **13**, 166 (1880); Wyckoff and Baker, *Am. J. Roentgenol. Radium Therapy*, **22**, 551 (1929); Jodlbauer and Tappeiner, *Ber.*, **38**, 2602 (1905); Jodlbauer, *Z. physik. Chem.*, **59**, 513 (1907); Roseveare and Olson, THIS JOURNAL, **51**, 1716 (1929); Roseveare, *ibid.*, **52**, 2617 (1930); Dhar, *J. Chem. Soc.*, **111**, 707 (1917); Kastle and Beatty, *Am. Chem. J.*, **24**, 182 (1900); Oberhauser and Schormüller, *Ann.*, **470**, 111 (1929); Dhar, *J. Chem. Soc.*, **111**, 690 (1917); Winther, *Z. wiss. Phot.*, **7**, 409 (1909), **8**, 197, 237 (1910).

[3] Jaeger and Thomas, *Proc. Acad. Sci. Amsterdam*, **21**, 693 (1919).