to remain in a vacuum desiccator overnight then extracted with 25 ml. of boiling xylene. The resulting solution was set in a warm place and evaporated. A crystalline residue resulted weighing 1.5 g. (12%). It melted at 151° (cor.) after recrystallization from xylene. No other crystalline product could be isolated.

Anal. Calcd. for $C_{15}H_{16}N_2O_4$: C, 62.50; H, 5.56. Found: C, 62.29; H, 5.32.

Summary

1. The reactions of 2-pyridone were studied with the objective of finding the best route to α-amino-β-(N-2-pyridone)-propionic acid, an analog of leucenol. The addition of 2-pyridone to α-acetamidoacrylic acid, followed by hydrolysis of the adduct, resulted in the product desired and provided the procedure for the successful synthesis of leucenol.

2. Other reactions of 2-pyridone which were explored during this investigation were numerous. β-(N-2-Pyridone)-propionic acid upon treatment with bromine and phosphorus gave β-(3,5-dibromo-N-2-pyridone)-propionic acid. 2-Pyridone gave the expected N-substituted products upon condensation with chloroacetaldehyde and bromopyruvic acid. It added to butadiene sulfone.

3. An extensive study was made of the condensation product of sodium 2-pyridone with α,β-dibromopropionic acid. The product was water soluble and contained ionizable bromine. It could be made more advantageously from 2-pyridone and α-bromoacrylic acid.

4. The 2-pyridone α-bromoacrylic acid adduct reacted with ammonia to give α-(N-2-pyridone)-β-aminopropionic acid or with aqueous alkali to give the corresponding β-hydroxy compound. Upon reduction with hydrogen and palladium-charcoal catalyst two moles of hydrogen were absorbed and the piperidone analog resulted as shown by treatment with ammonia to give α-(N-2-piperidone)-β-aminopropionic acid which was also made by the reduction of the α-(N-2-pyridone)-β-aminopropionic acid. When the adduct was reduced with hydrogen and platinum oxide as a catalyst, four moles of hydrogen were absorbed and α-hydroxy-β-piperidinopropionic acid was the product as shown by synthesis from piperidine and α-hydroxy-β-chloropropionic acid or from piperidinoacetaldehyde through the cyanohydrin. The mechanism of these transformations is discussed.

5. The 2-pyridone α-bromoacrylic acid adduct was titrated as a monobasic acid. With one molecule of silver oxide it yielded a betaine and with one-half mole of silver oxide a betaine hemihydrobromide. The infrared spectra of betaine hydrobromide and betaine compared closely with those of the 2-pyridone α-bromoacrylic acid adduct and the hydrobromide-free analog, thus showing similar groupings. The structure of the adduct is postulated as an ethylene-immonium bromide which permits a satisfactory explanation of all the experimental facts.

URBANA, ILLINOIS RECEIVED MAY 21, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

An Improved Apparatus for the Study of Reactions in Liquid Ammonia[1,2]

BY GEORGE W. WATT AND C. W. KEENAN[3]

Apparatus of the type described by Johnson and Fernelius[4] and modified extensively by Watt and Moore[5] for the conduct of reactions in liquid ammonia at its boiling point involves two serious shortcomings. Neither the original nor the modified apparatus provides for (a) the possibility of conducting titrations in a closed system (a procedure frequently advantageous in establishing the stoichiometry of reactions of liquid ammonia solutions of alkali and alkaline earth metals), or (b) the substantially quantitative removal of solid reaction products following *in situ* filtration and washing, without exposure of these products to the atmosphere. Both of these objectives are realized through use of the apparatus described in the present paper.

Two relatively simple reactions were chosen to demonstrate the operability of the equipment, *i. e.*, the reduction of ammonium bromide and silver(I) bromide with liquid ammonia solutions of potassium.[6] These cases show that the equipment described below permits one to exercise close analytical control over all reactants and products, including gaseous products; the importance of so-doing has been emphasized elsewhere.[7]

Experimental

Apparatus.—The apparatus designed to meet the needs indicated above is shown in Fig. 1. In general, this equipment is similar to that described by Watt and Moore[5]; consequently only the improvements will be pointed out here.

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[1] The major part of this work was done under the sponsorship of the Office of Naval Research, Contract N6onr-26610.

[2] The liquid ammonia employed in these studies was generously supplied by E. I. du Pont de Nemours and Company.

[3] Present address: Department of Chemistry, The University of Tennessee, Knoxville, Tennessee.

[4] Johnson and Fernelius, *J. Chem. Education*, **7**, 981 (1930).

[5] Watt and Moore, THIS JOURNAL, **70**, 1197 (1948).

[6] Several investigators have shown that silver(I) salts other than the bromide are reduced to elemental silver by the action of liquid ammonia solutions of alkali and alkaline earth metals [*cf.*, Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925); Burgess and Smoker, *ibid.*, **52**, 3573 (1930); *Chem. Revs.*, **8**, 265 (1931); Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **A154**, 1 (1931); Burgess and Smoker, THIS JOURNAL, **59**, 459, 462 (1937)].

[7] Fernelius and Watt, *Chem. Revs.*, **20**, 202, 216 (1937).

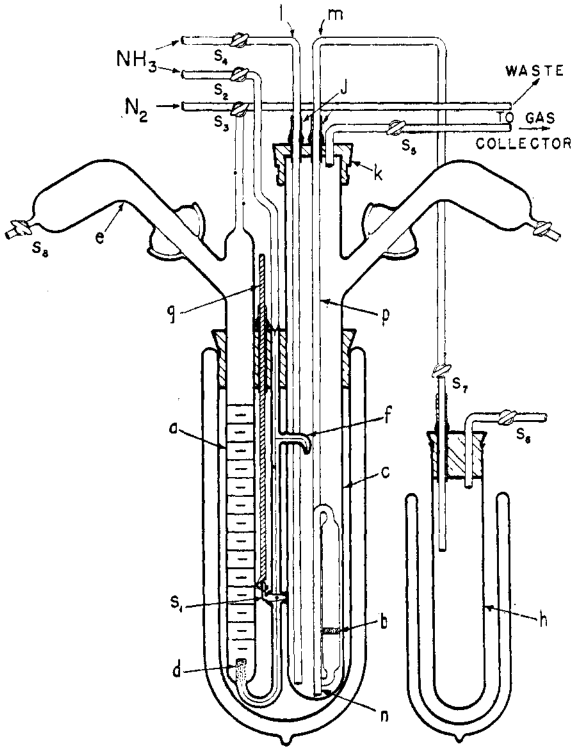

Fig. 1.

The novel features are the buret a and the internal in-line filter[8] b. Both the buret and the main reaction cell c are provided with addition bulbs connected by ball-socket joints held by spring clamps (not shown). In actual operation, ammonia is condensed in the buret until it is approximately one-half full, a known weight of alkali metal[9] is added from tube e, the solution is stirred by a stream of ammonia through the fritted glass filter[10] d, and sufficient additional ammonia is then condensed in a to give a metal solution of the desired concentration. Stopcock s_1 is closed and ammonia is condensed in c, which contains the substance which it is intended to bring into reaction with the metal solution.

Titrations with metal solutions are conducted as follows. With stopcock s_5 open, a positive pressure of dry oxygen-free nitrogen is exerted (through stopcock s_3) upon the surface of the metal solution in a. While the solution (or suspension) in c is stirred by a slow stream of ammonia gas, stopcock s_1 is opened and metal solution is delivered dropwise into c *via* the capillary delivery tip f, and at the same time the metal solution is filtered through d. Addition of metal solution may be interrupted upon the appearance in c of a color change, a precipitate, the beginning or cessation of gas evolution, or the first appearance of the characteristic blue color denoting the presence of excess metal solution.

[Stopcock s_1 is submerged in the coolant ammonia contained in the outer Dewar flask and is lubricated with Dow-Corning high vacuum grease. This stopcock is held in place by a spring clamp (not shown) and is manipulated by means of the metal rod g which is connected through a glass ring sealed onto the handle of the stopcock s_1. This rod extends through a glass sleeve in the rubber stopper and the closure between rod and sleeve is made with rubber tubing.]

Upon completion of a reaction that yields a solid product, filtration, washing, and collection of the solid are accomplished as follows. With controlled reduction of the pressure in tube h (evacuated *via* stopcock s_6), stopcock s_7 is opened and the contents of c filtered through b. The solid on the filter b is washed with fresh portions of ammonia successively condensed in c and drawn over through b as described above.[11] At the same time, the filtrate and washings are collected quantitatively in h. *While the solid on the filter is still wet with ammonia*, cap k (together with tubes l, m, and the gas exit tube) is removed from reaction cell c and, with stopcock, s_7 open, a small rubber cap (small bore pressure tubing closed at one end with a screw clamp) is quickly placed over the intake end of the filter tube, *i. e.*, at n. Tube m is then broken off at point p, attached to the vacuum line at point p, evacuated for a few minutes, and sealed off just above n. Following thorough evacuation to remove excess ammonia, tube m is sealed off between p and the top of the filter tube, and transferred to a dry box for all subsequent manipulations. Thus the solid sample is isolated without exposure to the atmosphere.[12]

The cap k is a rubber stopper bored out to fit over the tube c and held firmly in place by a metal collar (not shown) which is tightened with a screw. This type of cap obviates use of a thick stopper which would restrict the side-to-side movement of tubes l and m which are connected through k by means of rubber-to-glass seals which are kept gas-tight by means of spring clamps (not shown).

Titration of Ammonium Bromide Solution with Potassium Solution.—Weighed samples of am-

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(8) Ace Glass, Inc., Cat. No. 8570, filter tube, porosity C or D.

(9) The metal is cut under dry xylene, so that only freshly cut surfaces are exposed. While still wet with xylene, the metal is transferred to tube e while a current of dry ammonia gas is admitted *via* stopcock s_8. The xylene is volatilized in the ammonia gas stream, tube e is tightly stoppered, stopcock s_8 is closed, and the tube and its contents are weighed. Thereafter, tube e is attached to the side-arm on buret a which is previously flushed out with dry ammonia gas.

(10) Ace Glass, Inc., Cat. No. 8575, filter tube, porosity C.

(11) An alternative procedure is used with very finely divided solids which tend to clog the filter medium. The initial reaction is conducted with filter b raised upward in c so that the intake tip of the filter is above the level of the solution in c. The solid is allowed to settle, filter b is lowered carefully and the supernatant solution is drawn off with minimum disturbance of the settled solid. Thereafter, the solid is washed several times by condensation of fresh ammonia, settling, and decantation, before the bulk of the solid is finally drawn over onto the filter.

(12) While this procedure may appear to involve risk of exposure of the sample to the atmosphere, samples of highly pyrophoric metals which react violently upon the slightest exposure have been handled in this manner without any evidence of atmospheric oxidation.

monium bromide dissolved in approximately 50 ml. of liquid ammonia in c were titrated with potassium solutions of known concentration delivered from the calibrated buret a. The first appearance of a permanent blue color (characteristic of solutions of metals in ammonia) was taken as the end-point. Data for two such titrations are given in Table I (Expts. 1 and 2).

TABLE I

REDUCTION OF AMMONIUM BROMIDE AND SILVER(I) BROMIDE

Expt.	Substance	Reactants, g. Measured	Reactants, g. Calcd.[a]	Products Measured	Products Calcd.[a]	Acctd. for, %
	NH_4Br	1.0061				
1	K	0.397[b]	0.402			99
	H_2			109 cc.	115 cc.	95
	NH_4Br	1.0518				
2	K	0.418[b]	.420			100
	H_2			119 cc.	120 cc.	99
	AgBr	.3173				
3	K	.0667[b]	.0660			101
	Ag			0.1818 g.	0.1822 g.	99.8
	AgBr	.2877				
4	K	.0598[b]	.0599			100
	Ag			0.1646 g.	0.1653 g.	99.6

[a] Calcd. on the basis of the weight of ammonium bromide or silver(I) bromide used. [b] Measured as a portion (15–20 ml.) of a known volume (25–30 ml.) of potassium solution containing a weighed quantity of potassium.

Reduction of Silver(I) Bromide with Potassium.—Solutions containing known weights of silver(I) bromide were similarly titrated with potassium solutions. In these cases, however, the end-point could not be detected as indicated above, owing to the presence of the black finely divided precipitate of elemental silver. Consequently, a calculated volume of potassium solution was added, the precipitate allowed to settle, and drops of potassium solution were added to the clear supernatant solution until there was no further evidence of reaction. The combined supernatant solution and washings gave a negative test for silver ion. The resulting data are shown as Expts. 3 and 4, Table I.

Summary

An improved apparatus for the conduct of reactions in liquid ammonia at its boiling point has been described, and its utility demonstrated. This apparatus provides for titrations employing liquid ammonia solutions of metals and permits one to carry out filtration and purification operations at the boiling point of the solvent.

It has been demonstrated that silver(I) bromide is reduced to elemental silver by reaction with solutions of potassium in liquid ammonia.

AUSTIN, TEXAS RECEIVED MARCH 25, 1949

NOTES

Preparation of Radioactive Cyanide from Carbon Dioxide

BY RICHARD ABRAMS

For synthesis of labeled compounds it is often necessary to convert $BaC^{14}O_3$ to $HC^{14}N$. Available methods treat carbon dioxide with ammonia and potassium metal[1] (yield is a sensitive function of experimental conditions[2]), or treat barium carbonate with sodium azide[3] (yields are low in our experience). A method which has been found to be very satisfactory is based upon the reduction of carbon dioxide to carbon with magnesium powder,[4] and the conversion of amorphous carbon to hydrocyanic acid with ammonia gas at 1000°.[2,5,6] Yields are usually between 60 and 70% and not particularly dependent upon carbon dioxide pressure or magnesium excess.

In a typical experiment, carbon dioxide was liberated into a vacuum system from 1.1 mmoles. of barium carbonate by mixing with 1.6 g. of lead chloride and heating with a micro-burner.[7] Traces of water were removed by sublimation at −80°. The carbon dioxide was then admitted to a quartz tube containing 2.5 mmoles. of magnesium powder in a thin-walled iron thimble. The tube was heated rapidly with an oxygen flame until the thimble glowed red, and reaction began as noted by the sharp pressure drop. Intermittent heating was continued until the pressure remained constant. The contents of the thimble were washed with 1 *M* hydrochloric acid and with water, transferred as a slurry to a quartz boat, and dried under an infrared lamp. The yield was 0.76 mmole. of carbon which was 89% pure. Based upon the residual pressures of condensable and non-condensable gases and the acetylene liberated upon wetting the reaction mixture, the 30% loss consisted of approximately 5% unreacted carbon dioxide, 10% carbon monoxide, and 15% magnesium carbide.

The boat containing the carbon was placed in a quartz tube surrounded by an electric furnace. Ammonia gas was allowed to flow directly from the tank through the quartz tube and out through a wash bottle containing a 10% excess of 0.1 *M* sodium hydroxide. When all the air had been displaced by ammonia, the furnace was turned on so that the temperature rose to 1000° in thirty minutes, and stayed between 1000° and 1100° for two and one-half hours. All the hydrocyanic acid formed was carried out by the ammonia which flowed through the tube continuously at a

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(1) Cramer and Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(2) Loftfield, *Nucleonics*, **1**, 54 (1947).

(3) Adamson, THIS JOURNAL, **69**, 2564 (1947).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, England, 1925, Vol. 6, p. 71.

(5) Mellor, *ibid.*, 1924, vol. 5, p. 827.

(6) Cramer, Thesis, Harvard, 1941.

(7) Zwiebel, Turkevich and Miller, THIS JOURNAL, **71**, 376 (1949).