first determination, namely, +0.138 volt, thus placing arsenic between hydrogen and copper in the electromotive series.

2. Overvoltage.

The overvoltage of hydrogen on arsenic was determined by measuring the back e. m. f., or polarization, of a cell which consisted of a platinum anode, an arsenic cathode made as described above, and a *N* sulfuric acid electrolyte. The area of each electrode was one square centimeter. A gradually increasing e. m. f. was applied to these electrodes until a milliammeter indicated that current was just beginning to flow through the cell, showing that decomposition of the electrolyte had just begun. The polarization of the cell caused by this impressed e. m. f. was measured and by means of an auxiliary calomel electrode the anode and cathode polarizations, or overvoltages, were determined separately. Measurements were made by both the open and closed circuit methods. In the former the back e. m. f. is measured while the circuit furnishing the applied e. m. f. is open. It is necessary to make the readings very quickly because depolarization begins as soon as the circuit is broken. In the closed circuit method the arm of the auxiliary electrode vessel is drawn out at the end to a small tube which is bent up to a horizontal position and placed so that it almost touches the cathode. In this way the internal resistance of the electrolyte is largely eliminated and the potential between the cathode and the calomel electrode can be measured without breaking the main circuit. The value for the overvoltage of hydrogen on arsenic obtained by the open circuit method was 0.379 volt, while that by the closed circuit method was 0.478 volt.

This work was suggested by Dr. E. K. Rideal and carried out under his direction. The author wishes to take this opportunity to thank him for his many helpful suggestions and criticisms.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS.]

THE LIQUID AMMONIA-SODIUM METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS.

BY F. B. DAINS AND R. Q. BREWSTER.

Received May 27, 1920.

The liquid ammonia-sodium method for the determination of halogens in organic compounds was first published by Chablay.[1] This method had been independently developed in this laboratory, as the result of some observations by Dr. H. P. Cady, and was later published by Dains,[2] Vaughan and Janney. The process consists in dissolving 0.1 to 0.2 g. of substance, accurately weighed, in 30 to 50 cc. of liquid ammonia and

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[1] *Ann. chim. phys.*, [9] 1, 469–519 (1914).

[2] THIS JOURNAL, 40, 936 (1918).

treating the solution with small pieces of clean metallic sodium until the blue color formed in the solution persists for $^1/_2$ hour. The ammonia is then allowed to evaporate and the residue of sodium halide is taken up in water and the halogen content determined by any of the ordinary methods;[1] gravimetric analyses give the most accurate results, especially if the solutions are highly colored. The chief advantage of this method is that it is quite rapid and much more convenient than the Carius method.

Recently C. W. Clifford[2] made an investigation of the accuracy of this method and reported the results of the analysis of 5 halogen-containing organic compounds.

The first, carbon tetrachloride, gave both qualitative and quantitative evidence of the formation of cyanides. The second, hexachloroethane, also showed the presence of cyanides but not in sufficient amount to interfere with the quantitative determination. The other 3 compounds, which were not named, were evidently cyanide-free.

In the summary of the article the statement is made, "Cyanide is formed in many cases by the treatment of organic compounds with sodium in liquid ammonia."

Since Chablay had not mentioned the cyanide formation and its presence had not been noted in the relatively large number of analyses made in this laboratory, it seemed advisable to follow up this interesting observation of Clifford and to ascertain under what conditions it would be formed in sufficiently large amounts to interfere with the halogen determination. Consequently, a study of the action of sodium in liquid ammonia was made on a series of substances representing various classes of organic compounds. The procedure was as follows.

Unweighed samples of about 0.5 to 1.0 g. of each of these substances were dissolved in about 50 cc. of liquid ammonia and small pieces of sodium were added until the permanence of the blue color in the solution showed that an excess of sodium was present. After evaporation of the ammonia the residue was dissolved in water and qualitative tests for cyanides were applied. The prussian-blue test was selected because of the ease with which it will detect very small quantities of cyanides. Throughout the entire list of qualitative tests made the formation of prussian blue was either very intense or nil. Some of the materials examined contained halogens while others were halogen-free. The following table of data shows the results obtained from the 123 substances examined.

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[1] THIS JOURNAL, 41, 1051 (1919).

[2] *Ibid.*, 41, 1051 (1919).

Formation of Cyanides on Treatment with Liquid Ammonia and Sodium.

Negative results were obtained with the following:

Aliphatic Series.

- Hydrocarbons
  - Gasoline
  - Amylene
- Alkyl Halides
  - Methyl iodide
  - Ethyl iodide
  - Propyl bromide (*iso*)
  - Propyl bromide (*normal*)
  - Propyl chloride (*normal*)
  - Butyl iodide (*normal*)
  - Ethylene dibromide
  - Iodoform
  - Hexachloro-ethane
  - Methylene iodide
- Alcohols
  - Methyl alcohol
  - Ethyl alcohol
  - Propyl alcohol (*normal*)
  - Propyl alcohol (*iso*)
  - Butyl alcohol (*normal*)
  - Amyl alcohol (*tert.*)
  - Allyl alcohol
  - Glycol
  - Glycerol
- Ethers
  - Diethyl ether
- Aldehydes and Ketones
  - Formaldehyde
  - Paraldehyde, $(CH_3CHO)_3$
  - Acetone
  - Butyrone, $(C_3H_7COC_3H_7)$
- Acids
  - Formic acid
  - Acetic acid
  - Monochloro-acetic acid
  - Monobromo-acetic acid
  - Trichloro-acetic acid
  - Oxalic acid
  - Lactic acid
  - Tartaric acid
  - Succinic acid
  - Alanine
- Esters
  - Ethyl formate
  - Ethyl chlorocarbonate
  - Ethyl acetate
  - Ethyl butyrate
  - Ethyl oxalate
  - Ethyl malonate
  - Ethyl acetoacetate
  - Ethyl nitrite
- Amines
  - Ethylamine hydrochloride
  - Methylamine hydrobromide
- Amides
  - Formamide
  - Acetamide
- Miscellaneous
  - Urea
  - *m*-Bromo-diphenyl-thiourea
  - *p*-Bromo-phenyl-allyl-thiourea
  - Urethane
  - Casein

Aromatic Series.

- Hydrocarbons
  - Benzene
  - Naphthalene
  - Toluene
  - Diphenyl
  - Pinene
- Halogen Compounds
  - Chlorobenzene
  - Bromobenzene
  - Phenyl iodide
  - Di-bromobenzene (1–4)
  - Benzyl chloride
  - Benzal chloride
  - *o*-Bromotoluene
- Azo Compounds
  - Azobenzene
  - Diazo-aminobenzene
  - Amino-azobenzene
- Aldehydes and Ketones
  - Benzaldehyde
  - Salicylic aldehyde
  - Anisic aldehyde
  - Quinone
  - Chloranil
  - Benzophenone

- Phenols, Alcohols, Ethers
  - Phenol
  - *p*-Bromophenol
  - Cresol
  - β-Naphthol
  - Benzyl alcohol
  - Benzyl ethyl ether
  - Phenetol
- Nitro Compounds
  - Nitrobenzene
  - *o*-Chloro-nitrobenzene
  - *p*-Bromo-nitrobenzene
  - *p*-Nitrotoluene
- Amino Compounds
  - Aniline
  - *p*-Bromo-aniline
  - Formanilide
  - Acetanilide
  - *p*-Bromo-acetanilide
  - *p*-Toluidine
  - β-Naphthylamine
  - Phenyl hydrazine
  - *p*-Phenylene-diamine hydrochloride
- Acids
  - Benzoic acid
  - *m*-Bromobenzoic acid
  - Salicylic acid
  - Sulfanilic acid
  - *o*-Toluic acid
  - Cinnamic acid
  - Dibromo-cinnamic acid
- Esters
  - Ethyl benzoate
  - Phenyl benzoate
  - Methyl salicylate
  - Phenyl salicylate
- Heterocylic Compounds
  - Pyridine
  - Quinoline
  - Isoquinoline
  - Antipyrine
  - Uric acid
  - Caffeine
  - Quinine sulfate

The following substances gave positive tests for cyanides.

- Chloroform
- Bromoform
- Carbon tetrachloride
- Chloral hydrate
- Bromal hydrate
- Ethylidene chloride
- Tetrachloro-ethylene
- Acetylene tetrachloride
- Methyl cyanide
- Benzyl cyanide
- Ethyl cyano-acetate

In the cases of chloroform, bromoform, carbon tetrachloride, chloral and bromal hydrates, the formation of cyanides may be easily explained by the assumption that the trivalent nitrogen has replaced 3 negative halogen atoms with the loss of hydrogen halide. It is well known that chloroform may be converted into potassium cyanide by treatment with ammonia and alkali even at ordinary temperatures.[1]

$$CHCl_3 + NH_3 + 4KOH = KCN + 3KCl + 4H_2O.$$

The presence of cyanides in the liquid ammonia solution of chloroform and sodium is hence to be expected. Bromoform, carbon tetrachloride, chloral hydrate and bromal hydrate resemble chloroform in this respect.

Methyl cyanide, benzyl cyanide and cyano-acetic ester evidently split off sodium cyanide directly.[2]

The formation of cyanides from ethylidene chloride, tetrachloro-ethylene, and acetylene tetrachloride is not so easily explained. Presumably

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[1] Richter-Spielmann, "Organic Chemistry," 1, 246 (1916).

[2] *Ber.*, **2**, 319 (1869); *J. prakt. Chem.*, **22**, 264 (1880); *Ann.*, **65**, 269 (1848).

this is accounted for, first, by the loss of hydrogen chloride from the molecule,[1] followed by absorption of ammonia and further loss of hydrogen chloride, giving a cyanogen compound. In these special cases, therefore, a modified method of analysis must be used in order to separate the cyanides and halides. The method developed by Clifford has been found to be satisfactory.

Quantity of Cyanide Formed from Halogen Compounds.

It was considered of interest to determine whether the amount of sodium cyanide produced under the conditions of the analysis was at all near the quantity called for by the following equations.

$$CHCl_3 + NH_3 + 4Na = NaCN + 3NaCl + 2H_2$$

$$CCl_3CHO.H_2O + NH_3 + 4Na = NaCN + 3NaCl + \text{Unknown substances.}$$

Accurately weighed samples of chloroform, bromoform, iodoform and chloral hydrate were dissolved in liquid ammonia and treated with a slight excess of sodium. After the ammonia had evaporated the residue was dissolved in water and the quantity of cyanides formed determined by titration to faint turbidity with standardized silver nitrate solution in the weakly alkaline solution. The following table shows the percentage yield of sodium cyanide calculated for the theoretical yield according to the above equations.

YIELD OF CYANIDES.

Substance.	1. %.	2. %.	3. %.
Chloroform	48	31	33
Bromoform	30	36	24
Iodoform	0	0	0
Chloral hydrate	16.7	16.5	19.7

It is apparent that the quantity of sodium cyanide found is quite variable even under conditions which were believed to be very nearly the same. This statement was also made by Clifford, though no experimental evidence was given. The amount of cyanides formed might be increased or decreased by modifying the conditions of the analysis but no such effort was made.

Quantitative Analysis of Typical Organic Halogen Compounds.

The rather large list of qualitative experiments has shown that cyanides are formed to interfere in the analysis only in a few special cases. The following list of quantitative determinations is given to show the adaptability of the method to the various classes of organic compounds.

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[1] It has been shown by Chablay and also in this laboratory that the liquid ammonia-sodium solution behaves like alcoholic potash toward an alkyl halide, giving an unsaturated compound as one of the products.

Substance.	Halogen. Found. %.	Halogen. Calculated. %.
Isopropyl bromide	65.30	
	64.91	65.04
N-Butyl iodide	68.51	
	68.80	69.00
Monochloro-acetic acid	37.58	
	37.25	37.53
Chlorobenzene	31.50	
	31.35	31.53
Bromobenzene	50.70	
	50.89	50.93
p-Bromo-acetanilide	37.36	
	37.72	37.40
o-Chloro-nitrobenzene	22.80	
	22.42	22.52
p-Chloro-aniline	27.92	
	27.78	27.81
p-Bromophenol	46.50	
	46.37	46.25
m-Bromobenzoic acid	40.10	
	40.12	39.80
Benzyl chloride	27.85	28.03
m-Bromo-diphenyl-thiourea	25.85	
	25.96	26.03
2-*o*-Chloro-phenylamino-5-methyl-dihydro-thiazole	15.43	
	15.47	15.67

Attempts at the Quantitative Determination of the Cyanide Radical in Organic Compounds.

Since it was shown that the cyanogen radical was split off the organic molecule in liquid ammonia solution by treatment with sodium, it was hoped that this behavior could be made the basis for a quantitative determination of cyanides in such compounds. Hence, samples of methyl cyanide and benzyl cyanide were subjected to analysis by the general procedure as used in the case of halogen compounds. The sodium cyanide formed was determined by titration with standardized silver nitrate solution.

	Found. % CN.	Calculated. % CN.
Benzyl cyanide	20.25	
	19.50	22.2
Methyl cyanide	9.45	
	10.20	
	12.50	
	11.70	63.4

These results indicate that such a procedure could not be utilized for the quantitative determination of organic cyanides. Benzyl cyanide was converted very largely into sodium cyanide, but in the experiments with methyl cyanide this reaction was greatly decreased. In the latter case the chief product of the reaction seemed to be ethyl amine, resulting from the reduction of the methyl cyanide presumably, according to the following equation,

$$CH_3CN + 4NH_3 + 4Na = C_2H_5NH_2 + 4NaNH_2.$$

The behavior of alkyl halides and other substances with liquid ammonia alone and also in the presence of sodium, is being studied and further results will be published later.

Summary.

1. It has been shown that the reaction between liquid ammonia, sodium and organic compounds, leads to the formation of cyanides only in a few special cases whose nature has been discussed.

2. A list of quantitative determinations of halogen in various classes of organic compounds has been given which will supplement those formerly published by us and by Chablay.

3. Application of this method to the quantitative determination of cyanides in organic compounds met with no success.

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[CONTRIBUTION FROM THE PHYSICS LABORATORY, STATE UNIVERSITY OF IOWA.]

THE VAPOR PRESSURE CURVES OF SOLID AND LIQUID SELENIUM NEAR THE MELTING POINT.

BY L. E. DODD.

Object and Scope.

The object of this investigation has been to determine by the method of molecular flow the saturated vapor pressure of selenium in the vicinity of the melting point. This required the determination of both the sublimation curve of the crystalline solid and the vaporization curve of the liquid. Further, the aim has been to find from these data values for some of the physical constants of selenium near its melting point.

Molecular Flow of Gases and Knudsen's Equations.

Knudsen's[1] equations for resistance to molecular flow of gases are, for an aperture in a thin partition,

$$W_1 = \sqrt{2\pi}/A_1 \qquad (1)$$

and for a tube

$$W_2 = {}^3/_8\sqrt{\pi/2}\int^L O/A_2^2\,\mathrm{d}l \qquad (2)$$

where l is length of tube, O is circumference, and A_2 cross-sectional area, which may be variable.

[1] Knudsen, *Ann. Physik.*, 28, 75, 999 (1909).