the mixtures form precipitates of hydrous iron (III) oxide on standing. The Job method may be applied successfully where other equilibria in solution are involved but any such sol formation makes uncertain the comparison and interpretation of absorption data for mixtures of varying concentrations.

Just recently, Babko's experiments on iron–salicylic acid systems, which might be expected to be closely analogous to the sulfosalicylic acid system, have been reported.[8] He found FeR^+ (violet) in acid solution, then FeR_2^- (red), and finally $FeR_3^{=}$ (yellow) at about *p*H 10, but abstracts available do not indicate what corrections were made for hydrolysis or dissociation.

Experiments are now under way to extend transmittance measurements on the iron–sulfosalicylate systems to the ultraviolet region in an attempt to determine concentrations of the various species, especially $FeOH^{++}$, so that their effects may be measured.

Effect of Temperature.—The instrument used is such that accurate control of temperature is not possible, but approximate measurement of the temperature effect showed that increased temperatures increase the extent of complex formation. The per cent. transmittance decreased about 7% on heating from 20 to 40°. A thermostated absorption cell has now been built so that the temperature effect may be measured more accurately in an attempt to determine the extent of dissociation of the complex.

The authors wish to express their appreciation to Mr. Leland L. Antes, Microscopy Specialist, Bureau Engineering Research, University of Texas, for his assistance in connection with use of the spectrophotometer.

Summary

1. Spectrophotometric studies of complex formation between iron(III) and sulfosalicylic acid were made over a *p*H range of 1 to 9.

2. In strongly acid solutions (to *p*H 2.4) iron (III) and sulfosalicylic acid react in a 1:1 ratio to form a violet complex. Stability of the complex is a function of the acidity.

3. Measurements at higher *p*H values indicate complexes of other mole ratios, but accurate formulas could not be determined from ordinary concentration measurements.

AUSTIN, TEXAS RECEIVED JUNE 30, 1947

[8] Babko. *J. Gen. Chem.* (*U. S. S. R.*), **15**, 745 (1945); *C. A.*, **40**, 7042 (1947).

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

Some Reactions of Trisodium Monobismuthide in Liquid Ammonia[1,2]

BY GEORGE W. WATT AND THOMAS E. MOORE[3]

Although numerous intermetallic compounds of the alkali and alkaline earth metals have been prepared in liquid ammonia, the literature provides very little information concerning their reactions in this medium.[4] The present paper is concerned with the preparation of trisodium monobismuthide and the study of its properties as a reducing agent in liquid ammonia. Since there is no known method for the production of pure sodium bismuthate, it was of interest (particularly in view of the work of McCleary and Fernelius[5]) to determine whether trisodium monobismuthide could be oxidized to sodium bismuthate by treatment with molecular oxygen.

Trisodium monobismuthide was prepared by the reaction

$$BiI_3 + 6Na \longrightarrow Na_3Bi + 3NaI \qquad (1)$$

Treatment of the purified monobismuthide with molecular oxygen leads not to sodium bismuthate but rather to an insoluble mixture of bismuth(II) oxide, sodium hydroxide and sodium peroxide

$$4Na_3Bi + 5O_2 + 6NH_3 \longrightarrow 4BiO + 6NaOH + 6NaNH_2 \qquad (2a)$$

$$4Na_3Bi + 8O_2 \longrightarrow 4BiO + 6Na_2O_2 \qquad (2b)$$

In addition, the following reactions of trisodium monobismuthide have been observed.

$$Na_3Bi + 2Bi \longrightarrow Na_3Bi_3 \qquad (3)$$

$$2Na_3Bi + 6NH_4Br \longrightarrow 2Bi + 6NaBr + 6NH_3 + 3H_2 \qquad (4)$$

$$Na_3Bi + 3AgI \longrightarrow Bi + 3Ag + 3NaI \qquad (5)$$

$$Na_3Bi + BiI_3 \longrightarrow 2Bi + 3NaI \qquad (6)$$

$$2Na_3Bi + Bi_2O_3 + 3NH_3 \longrightarrow 4Bi + 3NaOH + 3NaNH_2 \qquad (7)$$

In the course of this work the conventional type of apparatus for the study of reactions in liquid ammonia at its boiling temperature has been modified extensively. The major improvements are concerned with techniques for filtration in a closed system.

Experimental

Apparatus.—With the exceptions noted below, the over-all details of construction and mode of operation of the equipment shown in Fig. 1 are similar to those described by Johnson and Fernelius.[6] Both reactors A

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[1] This work was supported, in part, by grants from The University Research Institute, Project No. 25.

[2] Presented at the Second Southwestern Regional Meeting of the American Chemical Society, Dallas, Texas, Dec. 13, 1946.

[3] Present address: Department of Chemistry, The Oklahoma A. and M. College, Stillwater, Oklahoma.

[4] Johnson and Fernelius, *J. Chem. Education*, **7**, 981–999 (1930).

[5] McCleary and Fernelius, THIS JOURNAL, **56**, 803 (1934).

[6] Johnson and Fernelius, *J. Chem. Education*, **6**, 445 (1929).

and B are provided with tubes b into which solid reaction products are transferred for removal from the system. These tubes are sealed off, evacuated, and opened in an inert atmosphere in a "dry box." At the start of a run, dry ammonia gas is admitted through stopcocks s_1 and s_2 as well as through tubes a in order to remove air more completely. Liquids may be added from g by means of an ammonia gas pressure applied at m, while gases may be added (with or without dilution with gaseous ammonia) *via* stopcock s_3.

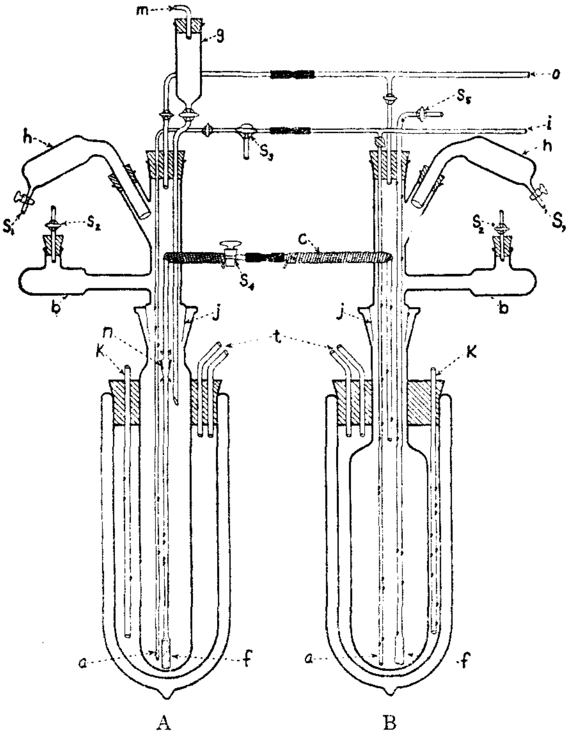

Fig. 1.

Reactor A is equipped with a fritted glass filter f attached by means of a ground glass joint n in order that change to filters of different porosity may be facilitated. The filter tube leads to reactor B through stopcock s_4 and a rubber connection tube.[7] The exposed connection tube between reactors A and B is wrapped with asbestos cord to provide the insulation necessary to prevent excessive "surging" during transfers. Filtration is accomplished by building up a gas pressure on the surface of the liquid in reactor A by admitting anhydrous ammonia gas through o (or less satisfactorily through stopcock s_1 or s_2) with stopcock s_4 open. Following filtration, solids remaining in reactor A may be washed by successive condensation of fresh portions of ammonia, followed by filtration. *Continuous washing* of a solid may be accomplished by balancing the rate of take-off through the filter with the rate of condensation of ammonia. This latter procedure is particularly advantageous when it is desired to extract an ammonia-soluble component of a mixture of solids in reactor A.

Reactor B may be made substantially identical with A although, as represented in Fig. 1, B does not include provision for addition of liquid reactants nor for interchangeable fritted glass filters. The filter tube shown for reactor B also differs in that it is supported through the rubber stopper at the top of the reactor rather than through a ring seal. This arrangement is shown for the reason that it is somewhat more flexible and less readily subject to breakage. For certain purposes, it is convenient to eliminate the fritted glass filter, f, in reactor B and to remove a slurry *via* the open tube through stopcock s_5 and into an external filter of the type shown in Fig. 2. This consists of a glass filter crucible r (having an extra fine porosity fritted glass filter plate) supported in a Dewar test tube w and connected to the tube bearing stopcock s_5 (Fig. 1) *via* a rubber connection e which carries a screw clamp d. With the screw clamp and stopcocks s and s_5 open and s′ closed, the pressure is lowered by a vacuum pump attached at x. After the insoluble material has been collected on the filter, washing is accomplished by means of successive fresh portions of liquid ammonia condensed in reactor B and subsequently drawn over into the external filter. Ammonia collected in the Dewar test tube is removed under reduced pressure *via* s or allowed to escape *via* the tube which bears stopcock s′ and which is connected to an ammonia absorber. Finally, s, s′, and d are closed, the entire assembly is detached and transferred to a "dry box" for removal of the solid on the filter and/or the residue in the Dewar test-tube.

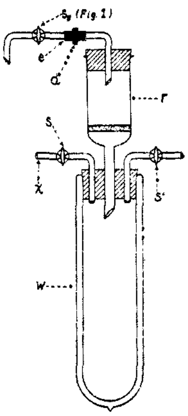

Fig. 2.

Numerous modifications of this equipment have been employed and are more or less obvious. Particular attention is called to the possibility of providing a third reactor which permits preparation, in separate vessels, of two liquid ammonia solutions that may then be brought together in the central unit.

Materials.—All apparatus and materials were thoroughly dried before use.

Bismuth(III) Iodide.—This material was prepared by the method of Birchenbach[8] and purified by three sublimations in an atmosphere of carbon dioxide.

Anal. Calcd. for BiI_3: Bi, 35.43. Found: Bi, 35.41.

Preparation of Trisodium Monobismuthide.—The black insoluble monobismuthide was prepared by reducing 1.5046 g. of bismuth(III) iodide in about 35 ml. of liquid ammonia with 0.3675 g. (6.26 equivalents) of sodium. The reaction was strongly exothermal and intermediate brown and violet colors characteristic of the ammonia-soluble tri and pentabismuthides[9] were observed. Analysis of the thoroughly washed precipitate showed that the Na/Bi ratio is 3.3.[10] Only traces of iodide ion and nitrogen were detected.

In order to show that bismuth is the *primary* product of reduction of the iodide, 1.4747 g. of bismuth(III) iodide was reduced with 0.1821 g. (3.17 equivalents) of sodium. The ammonia-insoluble product was found to contain 96.2% bismuth (pyrophoric) and 3.1% sodium hydroxide. When the bismuth was treated in liquid ammonia with an excess of ammonium bromide to remove sodium hydroxide, the final product contained 98.2% bismuth (non-pyrophoric) and 1.6% sodium hydroxide. This product gave X-ray diffraction patterns (Cu K_α radiation) that showed exactly and only the

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(7) This and the other two rubber connections should be longer than shown in Fig. 1, in order to provide the flexibility necessary for tilting of the reactor during transfer of solid samples from the bottom of the reactor to tube b.

(8) Birchenbach, *Ber.*, **40**, 1404 (1907).

(9) Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **A154**, 1 (1931).

(10) This value corresponds exactly to that found by Kraus and Kurtz [THIS JOURNAL, **47**, 43 (1925)] in their study of the reduction of bismuth(III) chloride. Zintl, *et al.*,[9] however, found a ratio of 3.0 using a potentiometric titration method. If sodium in excess of that required by the formula Na_3Bi is assumed to be present as sodium hydroxide resulting from the ammonolysis of sodium monoxide [*cf.* Kraus and White, THIS JOURNAL, **48**, 1781 (1926)], formed by surface oxidation of the sodium used, the composition of the insoluble product is 97.0% Na_3Bi and 3.4% NaOH.

lattice spacings and relative intensities characteristic of bismuth.[11]

Preparation of Bismuth(II) Oxide.—Trisodium monobismuthide from the reduction of 1.7185 g. of bismuth (III) iodide by 0.4337 g. of sodium was washed, suspended in liquid ammonia and treated with oxygen[12] for three hours. Addition of 2.29 g. of ammonium bromide[13] resulted in the liberation of 4.4 cc. of oxygen[14] (0°, 760 mm.) and the color of the solid changed from gray to jet black. Several independent sets of analytical data showed that the final solid product had the following percentage composition: BiO (96.5); NH$_3$ (0.4); NaBr (1.8); NaOH (1.8).

Bismuth(II) oxide reacts with atmospheric oxygen at a negligible rate at room temperature but is converted to bismuth(III) oxide upon gentle ignition. The black product failed to form an amalgam when agitated with mercury and was unchanged when heated to 300° *in vacuo*. X-Ray diffraction patterns showed the presence of only a trace of bismuth and the absence of other oxides of bismuth.

Conversion of Trisodium Monobismuthide to Trisodium Tribismuthide.—The trisodium monobismuthide prepared from 1.0154 g. of bismuth(III) iodide by reaction (1) was agitated in 30 ml. of liquid ammonia for two hours with 0.4231 g. of bismuth prepared by reduction of bismuth(III) iodide with three equivalents of sodium. The violet colored ammonia solution[9] was transferred from reactor A to reactor B and found to contain 0.1323 g. of bismuth. This corresponds to the utilization [in accordance with equation (3)] of 21% of the elemental bismuth used.

Reduction of Ammonium Bromide with Trisodium Monobismuthide.—Trisodium monobismuthide from 1.5137 g. of bismuth(III) iodide and 6.23 equivalents of sodium was suspended in 30 ml. of liquid ammonia and treated with 1.5060 g. of ammonium bromide. The insoluble products were a black precipitate and hydrogen (found, 80.6 cc.; calcd., 86.2 cc.). The precipitate was washed ten times and found to contain 98.3% bismuth and only traces of sodium and ammonia.

Reduction of Silver(I) Iodide with Trisodium Monobismuthide.—To 0.7880 g. of silver(I) iodide dissolved in 30 ml. of liquid ammonia was added 0.3040 g. of trisodium monobismuthide. A rapid exothermal reaction led to the formation of a heterogeneous mixture of a gray and a black solid which was washed thoroughly.

Anal. Calcd. for a 1:1 mixture of Ag and Bi: Ag, 61.3; Bi, 38.7. Found: Ag, 59.6; Bi, 37.5; Na, 0.6; I, 1.5.

Reduction of Bismuth(III) Iodide with Trisodium Monobismuthide.—In a similar manner, 1.3375 g. of bismuth(III) iodide was treated with 0.6242 g. of trisodium monobismuthide. The rapid exothermal reaction resulted in a black precipitate which was washed free of iodide ion.

Anal. Found: Bi, 96.7; NaOH, 2.8; NH$_3$, 0.4.

Reduction of Bismuth(III) Oxide with Trisodium Monobismuthide.—Bismuth(III) oxide (0.4900 g.) was agitated vigorously with 0.5800 g. of trisodium monobismuthide in liquid ammonia for three hours. The yellow color of the oxide was progressively replaced by a gray-black mixture of insoluble solids. Unreacted bismuthide was determined by addition of an excess of ammonium bromide, whereupon 40.0 cc. of hydrogen was liberated (see equation 4). By difference, this corresponds to the reduction of 43% of the oxide used. X-Ray diffraction patterns showed all of the lines characteristic of bismuth and bismuth(III) oxide[11] and only these lines.

Substantially identical results were obtained when the oxide was added slowly to a suspension of the tribismuthide in liquid ammonia.

Discussion

The formation of bismuth(II) oxide by oxidation of bismuth in a lower oxidation state has not been reported previously. In the present work, both physical and chemical evidence showed that the black solid did not contain more than traces of elemental bismuth, that the compound contained oxygen and that no other known oxide of bismuth was present.

Bismuth(II) oxide has been reported as a product of the reduction of bismuth(III) oxide with tin(II) chloride,[15,16] hydrogen or carbon monoxide,[17] and the reduction of bismuth(III) dioxyoxalate with carbon monoxide.[18-20] Early work purportedly leading to the formation of bismuth(II) oxide has been criticized by Neusser[21] who contends that the product is probably a mixture of bismuth(III) oxide and elemental bismuth. In the present work, it is significant that the observed properties of bismuth(II) oxide are in generally good agreement with those reported by earlier workers, and that the X-ray diffraction studies rule out the possibility of a mixture of the type suggested by Neusser except for the remote possibility that both of the components of such a mixture might be produced in an amorphous condition.

Summary

1. Improved apparatus and procedures for use in the study of reactions in liquid ammonia at its boiling temperature are described.

2. The reduction of bismuth(III) iodide by three equivalents of sodium in liquid ammonia leads to the formation of elemental bismuth which is essentially unreactive toward molecular oxygen in the same medium.

3. Bismuth(III) iodide is reduced to trisodium monobismuthide by six equivalents of sodium, and the monobismuthide reacts with molecular oxygen to form bismuth(II) oxide and a mixture of oxides of sodium.

4. The reducing properties of trisodium monobismuthide are demonstrated by its use in the partial reduction of bismuth to tribismuthide ion and bismuth(III) oxide to bismuth, and

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[11] Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

[12] In related experiments it was found that, under similar conditions, bismuth [from the reduction of bismuth(III) iodide with three equivalents of sodium] is not oxidized upon treatment with oxygen over a period of four hours, either in the presence or absence of water.

[13] Preliminary experiments showed that in addition to bismuth (II) oxide, the gross solid product contained sodium hydroxide and sodium peroxide, both of which were dissolved upon addition of ammonium bromide.

[14] Considerable variation in the volume of oxygen liberated reflected the comparative extent of occurrence of reactions 2a and 2b. *Cf.* Kraus and Parmenter, THIS JOURNAL, **56**, 2384 (1934).

[15] Schneider, *Pogg. Ann.*, **63**, 53 (1844); **68**, 49 (1846); **88**, **45** (1853).

[16] Muir, *J. Chem. Soc.*, **31**, 650 (1877).

[17] Muir, Hoffmeister and Robbs, *ibid.*, **39**, 21 (1881).

[18] Tanatar, *Z. anorg. Chem.*, **27**, 437 (1901).

[19] Hertz and Guthmann, *ibid.*, **53**, 63 (1907).

[20] Denham, THIS JOURNAL, **43**, 2367 (1921).

[21] Neusser, *Z. anorg. Chem.*, **135**, 313 (1924); **138**, 180 (1924).

the complete reduction of ammonium ion to hydrogen, silver (I) iodide to silver, and bismuth(III) iodide to bismuth.

AUSTIN, TEXAS RECEIVED JULY 3, 1947

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

The Catalytic Reaction of Hydrogen and Oxygen on Plane Faces of a Single Crystal of Copper[1]

BY HENRY LEIDHEISER, JR., AND ALLAN T. GWATHMEY

Introduction

The determination of the positions of different activity on a catalyst surface is a question of primary importance. The two great difficulties in determining these positions are the preparation of a surface of known structure and the development of a method for following changes in the structure as the reaction takes place.

Most studies made in the past on the activity of a solid catalyst surface have consisted of measuring the amounts of materials consumed and produced by powdered metal catalysts. Such catalysts generally consist of many crystals randomly arranged and exposing faces, edges and corners of many kinds. Measurements made on such materials are composite quantities and give little direct information about the reactivity of the various types of structure exposed.

In an effort to obtain simple, reproducible surfaces of known structure, large single crystals with surfaces prepared parallel to special planes were selected. Furthermore, previous studies with large single crystals[2] have shown that the rate of many surface processes varies with the crystal face exposed at the surface. Therefore in order to determine the influence of crystal plane on catalytic activity and to extend our knowledge of metal surfaces in general, studies have been made of the reaction of hydrogen and oxygen on several plane faces of a large single crystal of copper.

In the study of the reaction of gases on the surface of metallic crystals, it has been found that the reactions may be divided into two classes, those which readily produce rearrangements in the surface and those which do not, at least on a microscopic scale. The reaction of hydrogen and oxygen on copper belongs to the first class. The nature of the rearrangements produced by the action of hydrogen and oxygen will first be described, and then the measurement of rates on several faces will be presented. An important feature of these studies is the correlation between catalytic activity and surface structure which can be observed.

Method of Experiment

Preparation of Surface of Catalyst.—There is a tendency in catalytic studies to underrate the importance of the preparation of the surface. Very fine measurements are often of limited value because they are made on surfaces, about the structure and composition of which little is known. Emphasis was placed in these studies on the preparation of the surface.

Single crystals of copper in the form of rods, $^{5}/_{8}$ in. in diameter and 4 in. long, were grown by the method previously described.[2,3] For use in the studies of rearrangements, spheres were machined from the $^{5}/_{8}$ in. rods and polished mechanically and electrolytically. For the rate measurements thin slices, about $^{1}/_{8}$ in. thick and parallel to the (100) and (111) planes were cut from a 1-inch crystal. In order to assure that there could be no difference in the chemical composition of the two crystal faces on which rates were measured, a sphere was machined from a 1-inch rod, and two flat faces, one parallel to the (100) face and one to the (111) face, were cut on the sphere. This was done by the same method used in cutting the slices. Photographs of the several specimens are shown in Figs. 2 and 14. The flat faces for rate measurements were polished as follows. The face was mechanically polished with metallographic polishing papers nos. 1 through 0000, and after each paper it was electrolytically etched in the polishing solution at a current density of about 0.02 amp./sq. cm. for a sufficient length of time to remove the strained layer produced by the last mechanical polishing. The time varied from about thirty minutes after the no. 1 paper to about ten minutes after the last paper. After the last etching the surface was slightly roughened on a microscopic scale but plane on a macroscopic scale and in a strain-free condition. The final step consisted of polishing mechanically on a felt wheel moistened with levigated alumina. In order to prevent subsequent recrystallization of the surface it was necessary to keep the cloth wet, to operate the wheel at a slow speed of about 150 r.p.m., and to press the specimen only lightly against the felt. After the first treatment with the reacting gases, it was only necessary to repolish with the 0000 paper and alumina, or with alumina alone. The surface was swabbed with a soft tissue under a stream of water in order to remove traces of alumina. Surfaces prepared by this method gave essentially the same results as those prepared by careful electrolytic polishing but the method described above was generally used because of the tendency of large surfaces to become pitted during electrolytic polishing. In order to reduce oxide and remove any distortion in the surface, all crystals were annealed in hydrogen at 550° for at least sixteen hours immediately prior to study of rearrangements or measurement of rates of reaction.

The Study of Rearrangements.—Since the surface of a monocrystalline sphere of copper exposes every crystal plane in at least six places, the (100) face appearing six times, most of the rearrangement studies were carried out on $^{5}/_{8}$ in. spheres. Also the symmetry of the patterns on a sphere make it easy to identify the location of the crystal faces. For the study of rearrangements the sphere was supported, generally with shaft downward, within the bulb of a glass apparatus connected with suitable inlet and exit tubes. The sphere was placed in the apparatus through a ground glass joint at the top and was suspended from the upper half of the joint by means of a no. 20 B. and S.

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[1] This work was supported by a grant from the Research Corporation.

[2] See Leidheiser and Gwathmey, *Trans. Electrochem. Soc.*, **91**, (1947) [printed as Preprint 91-6, but not yet published] for a résumé of previous studies with massive single crystals.

[3] Gwathmey and Benton, *J. Phys. Chem.*, **44**, 35 (1940).