in the reaction tube. When allowed to warm to room temperature, the solid began to evolve H_2; on heating to 80° it evolved 6.95 mmoles of condensable gas and 0.99 mmole of H_2. A white, extremely reactive solid remained in the tube. A 26-mg sample of this solid was treated with 6 M HCl; 0.83 mmole of H_2 and 0.48 mmole of NaCl were identified.

The foregoing data which are representative of several runs can be interpreted in quantitative detail as shown in Figure 1A.

In a second run evidence for $Na[H_2B(CH_3)_2]\cdot$solvent as a stable solid at room temperature was obtained. A 1.54-mmole sample of $[(CH_3)_2B(NH_3)_2^+][H_2B(CH_3)_2^-]$ was allowed to react with 1.57 mg-atoms of Na in liquid ammonia at −45°. After removing the H_2 (0.71 mmole) and excess NH_3 as before, the solid which remained was dissolved in 5 ml of dry dimethyl ether, then the dimethyl ether was pumped off at −45°. The solid was then treated with another portion of dimethyl ether and the ether was removed as before. On warming to room temperature the solid evolved 0.21 mmole of H_2 over a period of 3 hr. After volatiles were removed, a 19-mg sample of the solid was treated with 6 M aqueous HCl. A 0.44-mmole sample of H_2 was evolved and 0.22 mmole of NaCl remained. The foregoing data may be interpreted in quantitative detail as shown in Figure 1B.

An Attempt to Synthesize $Na[H_2B(CH_3)_2]$ Directly. The Reaction of NaH and $[HB(CH_3)_2]_2$ in Ether.—In a typical experiment a 10.8-mg sample of NaH (0.45 mmole) was placed in a reaction tube on the vacuum line, a 1.50-mmole sample of $(CH_3)_4B_2H_2$ and a 2.0-mmole quantity of diethyl ether were distilled into the tube, and it was allowed to warm to room temperature. After 1 hr all but a trace of the normally insoluble

NaH was dissolved in the ether, indicating complex formation. When the volatile materials were pumped off, a 3.50-mmole sample of volatile material was recovered (1.50 mmoles of $(CH_3)_4$-B_2H_2 and 2.0 mmoles of $(C_2H_5)_2O$). The solid remaining showed only diffuse lines of NaH. The formation process is clearly reversible under the conditions used.

The Synthesis of $(CH_3)_2BHNH_3$. The Reaction of Tetramethyldiborane and Ammonia in Ethereal Solvents.—A 1.66-mmole sample of pure $(CH_3)_2BH_2B(CH_3)_2$ was treated in a reaction tube on the vacuum line with 13.5 mmoles of dry $(CH_3)_2O$ for 1 hr, then a 13.5 mmole sample of NH_3 was added and the system was allowed to stand for 2 hr more at −78°. Excess ammonia and solvent were removed by pumping at −78° for 12 hr, at −45° for 3 hr, and finally at 0° for 1 hr. The product decomposed completely in 1 hr forming 3.24 mmoles of H_2 and 3.21 mmoles of $(CH_3)_2BNH_2$. Similar results were obtained using diethyl ether and tetrahydrofuran as solvents. In no case was a material obtained which was stable at room temperature.

Conductivity measurements were carried out by preparing the solute as above in the conductivity cell, removing ether and excess ammonia at −45°, then adding fresh, pure ammonia and measuring the conductivity at −35°. The equivalent conductance was 4 mhos in a concentration of 0.050 mole of $(CH_3)_2$-$BH_2NH_3/l.$ of NH_3. The solid is almost a nonelectrolyte, supporting the molecular formula.

Contribution from the Department of Chemistry,
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Reactions of the Metallic Sodium Surface with Atmospheric Gases[1]

By L. G. McKNIGHT[2] and L. O. BROCKWAY

Sodium metal surfaces, prepared by condensation of the metal under vacuum, have been exposed to water vapor, dried oxygen, moist CO_2, and dried and moist laboratory air at room temperature and at pressures between 10^{-3} torr and 1 atm. The surfaces were examined using the electron diffraction technique and Na_2O, NaOH, and Na_2CO_3 identified as the only initial reaction products. Oxygen was found to react with the metal surface to form Na_2O directly, and higher oxides of sodium did not appear under any of the reaction conditions.

I. Introduction

The reactions of metallic sodium with atmospheric gases have been observed since the discovery of the metal, and the literature concerned with these reactions is so extensive that only a few of the relevant papers are mentioned here.[3] However, the initial reaction products have not been established, and the identification of the initial reaction products on the metal surface exposed to reactive gas may help to indicate the mechanism by which the final products are formed.

The reaction of sodium with dry oxygen was discussed

by Cathcart, Hall, and Smith,[4] who postulated that the initial reaction product of the reaction is Na_2O but could not exclude the possibility that Na_2O_2 is formed at the oxide–oxygen interface. Their experiments, using carefully dried oxygen, showed that the reaction of the surface almost stopped after the formation of a layer of surface oxide calculated to be 1500 A thick. Trace amounts of nitrogen are said to affect the reaction.[5] Reactions of the surface with other atmospheric gases have not been studied under controlled conditions.

Electron diffraction investigations have been made of the reaction products of sodium by Yamaguchi.[6]

(1) This work is taken from a thesis presented by L. McKnight to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the Ph.D. degree, March 1961.

(2) Bell Telephone Laboratories, Inc., Murray Hill, N. J.

(3) A complete review of the properties and reactions of the metal has been published by M. Sittig, "Sodium, Its Manufacture, Properties and Uses," Reinhold Publishing Corp., New York, N. Y., 1956.

(4) J. V. Cathcart, L. L. Hall, and G. P. Smith, *Acta Met.*, **5**, 245 (1957).

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II. Experimental Section

A. Apparatus and Experimental Procedure.—The equipment used in the present investigation was an RCA EMD-2 electron diffraction unit modified so that the specimen and plate chambers were evacuated by separate pumping systems including liquid nitrogen cooled traps for rapid pumping of water vapor. Every effort was made to exclude water vapor from the instrument vacuum at all times, and some experiments were preceded by pumping times of many hours, extending in a few cases to 1 week. The remaining traces of water vapor were due in large part to evolution of water from surfaces within the specimen chamber; baking out of the specimen chamber was precluded by the design of the diffraction instrument. The minimum pressure achieved in the specimen section of the diffraction instrument during the present investigation was about 5×10^{-6} torr although pressures of 7–8×10^{-6} torr were normally reached after about 24 hr of pumping on the specimen chamber. During evaporation of sodium, the pressure in the specimen chamber rose to 2–4×10^{-5} torr and then fell rapidly.

The sodium was introduced into the diffraction instrument in an ampoule which could be broken by a mechanical motion through the vacuum wall. The metal was evaporated from the ampoule and condensed onto a surface in a layer estimated at 0.1 mm. Surfaces prepared on aluminum, brass, and palladium targets gave identical results. The prepared surfaces were exposed to atmospheric gases at room temperature (25°) and at total pressures between 10^{-2} torr and atmospheric pressure. Reaction times were between 10 sec and 5 min.

The production and reaction of the surfaces were divided into three stages. First, a fresh surface was prepared by condensing evaporated sodium onto the specimen stage, and the diffraction pattern from the surface was recorded on a photographic plate. Within 2 min of the time the surface was prepared, the electron beam was turned off and the specimen chamber was isolated from the vacuum pumps. Then, the reactive gas was admitted to the specimen chamber and allowed to react with the surface for the desired length of time. Finally, the valve to the vacuum pumps was reopened, and after about 1 min the pressure had fallen low enough to turn on the electron beam and the pattern from the surface was recorded.

Gases were introduced into the vacuum chamber from a gas bulb which was filled at atmospheric pressure. Gas pressures within the specimen chamber were determined by calculation from the relative sizes of the bulb and the specimen chamber.

B. Materials.—Matheson "prepurified" nitrogen rated at 99.996% (with 0.0008% of oxygen) was used in these experiments as a carrier gas for water vapor and as an inert standard gas for testing the gas-handling system. The gas was dried at atmospheric pressure by passing it through silica gel at liquid nitrogen temperature. Mass spectrographic analysis of nitrogen collected in this way showed both oxygen and water vapor to be less than 0.01 mole %.

In experiments involving moist nitrogen, water vapor was added to the gas by passing it at atmospheric pressure through water at 0°, thus adding 4.6 torr of water vapor or about 0.6% of the total gas pressure.

Cylinder oxygen of 99.3% purity with nitrogen as the principal impurity was used. It was condensed at atmospheric pressure and reevaporated before use. Mass spectrometric analysis of a sample of oxygen treated in this way revealed about 1% argon but was inconclusive as to the amounts of N_2 and CO_2 in the gas. Probably the oxygen contained small amounts ($\sim$1%) of nitrogen. The vapor pressure of CO_2 at the liquid oxygen boiling point ($-183°$) is given as 4×10^{-6} mm,[7] and serious contamination by this material is unlikely. Mass spectrographic data showed the amount of water vapor to be less than 0.04%, the limit of sensitivity of the instrument.

Matheson Bone Dry carbon dioxide (99.8%) was dried by passing it over silica gel at $-78°$. The vapor pressure of water

at this temperature is about 5×10^{-4} torr.[8] In the series of experiments involving moist CO_2, the gas was saturated with water vapor at 0°, giving a water vapor pressure of 4.6 torr or 0.6% of total gas pressure.

Laboratory air was dried by passing it through a trap at $-78°$.

C. Identification of the Reaction Products.—Phases present on the surface were identified by comparing the line spacing in the electron diffraction pattern with X-ray data from the ASTM X-ray data file. d values obtained from the data file were checked against the values calculated from the structures of the compounds where the structures were known. Surprisingly, the structure of anhydrous Na_2CO_3 is not known and in this case the data from the ASTM file were compared with powder patterns taken from Na_2CO_3 heated to temperatures between 200 and 500° to check the reliability of the Na_2CO_3 pattern in the file.

In electron diffraction the penetration of electrons into the specimen is limited to about 3×10^{-6} cm and most of the available intensity comes from within 10^{-6} cm of the specimen surface. Within this layer the diffraction pattern will reveal the presence of crystalline materials which represent amounts above about 5% of the total volume exposed to the beam. Smaller amounts of crystalline material would be easily detected if present on the surface of the specimen.

As might be expected, the intensities of lines derived from X-ray data did not correspond in all cases with those observed in the electron diffraction patterns from the surface. The principal difference observed during this investigation was in the pattern from anhydrous NaOH where the 002, 004, and 006 lines were considerably less intense in the electron diffraction patterns than in the X-ray data. All of the patterns from the condensed sodium surface were randomly oriented and no evidence of preferred orientation of reaction products was obtained.

III. Results

A. The Character of the Reactive Sodium Surface. —The surface produced by condensation of sodium ranged in color from brown to dark gray and was never smooth enough to present a shiny appearance. The thickness of the metal layer deposited during each evaporation is estimated at 0.1 mm. The electron diffraction patterns obtained by reflection from the metal surface usually showed the lines for polycrystalline sodium with a few additional lines due to NaOH or Na_2O or both also present. The patterns were clear and sharp in all cases with lines visible out to d values of 1.0 A and beyond. In one case a surface was obtained which showed only diffraction lines due to metallic sodium. This surface was prepared after more than 1 week of pumping on the specimen and plate chambers with the cold trap in the specimen chamber filled with liquid nitrogen throughout that time.

Most of the experiments performed during the present investigation were made on surfaces showing some contamination due to Na_2O or NaOH or both. Sodium hydroxide was the only contaminant observed when diffraction exposures were made using fresh photographic plates or when the inside of the specimen chamber had been recently exposed to moist air. In only a few cases was the amount of water vapor sufficient to produce NaOH lines of greater intensity than those of sodium.

Experiments showed that exposure of the surface to the vacuum in the diffraction instrument resulted in an

(7) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 43rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 2370.

(8) See ref 7, p 2361.

increase in the intensity of lines due to NaOH. Exposing the sodium surface to dried nitrogen under the experimental conditions produced about the same change as would have been produced under vacuum. In no case was the increase sufficient to produce NaOH lines of greater intensity than the strongest Na line.

B. Water Vapor.—In this series of experiments the surface was exposed for 1 min to a mixture of water vapor carried in prepurified nitrogen so that the water vapor pressure was about 0.6% of the total. The water vapor pressure was varied from 3×10^{-4} to 3×10^{-2} torr on different surfaces. The nitrogen pressure varied correspondingly from 5×10^{-2} to 5 torr. Surfaces treated in this manner were very similar despite the 100-fold variation in water vapor pressure, showing Na and NaOH lines of about equal intensity. Water vapor pressures above 3×10^{-2} torr were not used since the water vapor adversely affected the characteristics of the vacuum produced in the diffraction instrument.

C. Dried Oxygen.—In this series of experiments the surface was exposed to dried oxygen at pressures between 0.05 and 50 torr and for times between 10 sec and 5 min. There was considerable variation in the patterns taken from surfaces after supposedly identical experiments but some observations can be made. The principal effect was a great increase in the intensity of the lines due to Na$_2$O after exposure of the surface to oxygen, so that, in the case of surfaces exposed to oxygen pressures greater than 5 torr, the Na$_2$O lines were the strongest in the pattern. Some surfaces exposed to oxygen at 5 torr reacted to such an extent that sodium lines were no longer visible in the pattern, but a pattern from a surface exposed to the gas at 50 torr for 5 min showed strong sodium lines. In all cases, lines due to NaOH were observed in the pattern from the surfaces before and after the interaction with the gas, the intensity change being about what would be expected of the surface standing in the instrument vacuum.

In the experiments using oxygen pressures below 5 torr only the phases Na, Na$_2$O, and NaOH were observed. There were no extra lines and therefore no evidence of any other phase present on the surface. Oxygen pressures higher than 5 torr resulted in ignition of the hot sodium in the evaporator and contamination of the target surface with a crystalline reaction product which could not be identified despite a considerable literature search. Surfaces protected from the burning sodium, however, showed only lines due to Na, Na$_2$O, and NaOH.

D. Carbon Dioxide (99.4%) and Water Vapor (0.6%).—Carbon dioxide with 0.6% water vapor was introduced into the system at a total pressure of 5 torr. The failure of this gas mixture to produce any phase which could be identified as a carbonate prompted a series of experiments with this gas mixture in which the total pressure was varied between 0.05 and 50 torr with the water vapor pressure varying correspondingly between 3×10^{-4} and 3×10^{-1} torr. Reaction times were varied between 1 and 5 min. Surfaces exposed to the mixture at pressures less than 5 torr showed only lines due to Na and NaOH in the diffraction pattern. Only when the pressure of CO$_2$ reached 50 torr (with 0.3 torr of H$_2$O) did any trace of a carbonate appear when a single, very weak line showed up at the position expected for the strongest line in the Na$_2$CO$_3$ X-ray powder pattern. All of the patterns taken from the surface after introduction of the carbon dioxide water vapor mixture were clear and sharp, and all showed sodium as one of the principal phases present after the surface had been exposed to the gas mixture. Despite the overwhelming excess of CO$_2$ present in the specimen chamber, the principal observed change was the formation of NaOH in amounts which increased as the amount of water vapor increased.

E. Laboratory Air (Water Vapor $\sim$1%).—In this series of experiments the surface was exposed to laboratory air at pressures from 0.5 torr to 1 atm and for times from 10 sec to 5 min. The water vapor content of the air produced an increase in the amount of NaOH such that NaOH appears as the principal product in all of the patterns taken at pressures of 50 torr or less. This increase in the amount of NaOH on the surface was at the expense of the Na$_2$O, and lines due to Na$_2$O were not observed in patterns from surfaces after treatment with moist air, the observed change being entirely the production of NaOH to the extent that Na lines were not visible in patterns from surfaces exposed to air at pressures above 50 torr. Lines due to Na$_2$CO$_3$ appear in a pattern taken from a surface exposed to the laboratory air at 50 torr for 5 min. Patterns taken from surfaces exposed to air at a pressure of 1 atm were not sharp, owing to charging up of the surface, probably as a result of a thick layer of reaction products. NaOH lines are present in a pattern taken from a surface exposed to air at 1 atm for 1 min, but only blurred lines due to Na$_2$CO$_3$ were present after exposure of the surface at atmospheric pressure for 2 min.

IV. Discussion

Under the conditions used in the present investigation only three phases were observed on the sodium surface: Na$_2$O, NaOH, and Na$_2$CO$_3$, of which the last was only observed after extensive reaction had taken place. There were no extra diffraction lines and therefore no evidence of other reaction products on the metal surface. The clear, sharp patterns obtained from most of the surfaces after reaction would seem to preclude extensive amounts of undetected reaction products in the present series of experiments, and minute amounts of any crystalline materials on the surface would be easily identified. Only products present in amounts too small to form a crystal structure or minute amounts of amorphous reaction products would not be visible in the diffraction pattern. The surface was extremely sensitive to traces of water vapor, and sodium hydroxide was observed on virtually all of the surfaces produced during the investigation, the trace amounts of water vapor present in the diffraction instrument vacuum

being sufficient to produce the characteristic lines of the compound in less than 1 min. Oxygen containing 0.6% water vapor produced NaOH as the only reaction product visible on the surface, and even carbon dioxide containing 0.6% water vapor gave NaOH as the only product on surfaces when the reaction was not extensive.

The initial reaction product of sodium with dry oxygen is crystalline Na_2O, and the clear, sharp patterns from these surfaces would seem to preclude any appreciable amounts of noncrystalline materials on the metal surface. No trace of Na_2O_2 or higher sodium oxides was ever observed. The residual water vapor present under the driest conditions was revealed by small amounts of NaOH present on the surface, and it was probably variation in the trace of water vapor present which caused the variation in the extent of the reaction of the surface with oxygen. Dried air produced

about the effect which would be expected from its oxygen content, and the trace of CO_2 present did not affect the course of the reaction. Moist laboratory air, however, produced no oxide at all, only NaOH appearing in patterns from the surface. The formation of a crystalline carbonate is a very late stage in the surface reaction, even in the presence of an overwhelming excess of CO_2, and Na_2CO_3 was observed only on surfaces where extensive reaction had taken place. No trace of crystalline $NaHCO_3$ was observed.

Synthesis of Molybdenum and Tungsten Bronzes at High Pressure

BY T. A. BITHER, J. L. GILLSON, AND H. S. YOUNG

Molybdenum bronzes $Na_{0.90-0.97}MoO_3$ (cubic), $K_{0.89-0.93}MoO_3$ (cubic), $K_{\sim0.5}MoO_3$ (tetragonal I), and $Rb_{0.27}MoO_3$ (hexagonal), isotypic with known tungsten bronzes, have been prepared at 65 kbars pressure. The cubic and tetragonal phases are metallic conductors like their tungsten analogs, but the hexagonal bronze shows semiconductor behavior. In addition, an orthorhombic $Rb_{0.41-0.44}MoO_3$ (semiconductor) and the previously unreported cubic K_xWO_3 have also been made under the same conditions, as well as a monoclinic $Na_2Cr_3O_9$ phase (insulator).

Introduction

Although early workers[1,2] have indicated the preparation of nonstoichiometric alkali metal molybdenum bronze-type compounds M_xMoO_3, the first authenticated examples of these have only recently been reported by Wold, *et al.*,[3] who used an electrolytic reduction technique for their preparation. Products low in sodium or potassium ($x < 0.3$) with structures[4] not related to those observed in the tungsten bronzes were formed.

Molybdenum bronze phases with sodium, potassium, and rubidium, some of which are isotypic with known cubic, tetragonal I, and hexagonal tungsten bronzes, have now been prepared by reaction of alkali molybdate with molybdenum trioxide and molybdenum metal under high pressure. A monoclinic sodium and the heretofore unreported cubic potassium tungsten bronze have also been isolated. Extension to alkaline earth tungstates has given the previously reported

tetragonal I Ba_xWO_3 and Sr_xWO_3[5] and hexagonal Ca_xWO_3[6] phases. In the chromium system, a monoclinic $Na_2Cr_3O_9$ phase has been prepared.

Experimental Section

Preparation of Materials.—Syntheses were effected in a tetrahedral anvil press of National Bureau of Standards design[7] at pressures of 60–65 kbars, unless otherwise indicated. Pressure was calibrated on the basis of the electrical transitions for Bi (25.4 and 26.9 kbars), Tl (36.7 kbars), and Ba (59.0 kbars).[7] Temperatures were measured with Pt–Rh thermocouples uncorrected for pressure effects. The syntheses were carried out in cylindrical platinum containers (0.14 cm^3 volume) inserted into pyrophyllite tetrahedra. The platinum containers also served as heaters, and the thermocouples were adjacent thereto. An almost instantaneous quench to room temperature from the elevated reaction temperature was achieved by power cut off.

Mixtures of reagent grade alkali metal molybdate, molybdenum trioxide, and powdered molybdenum metal were blended according to the stoichiometry

$$xM_2MoO_4 + \frac{6-4x}{3} MoO_3 + \frac{x}{3} Mo \longrightarrow 2M_xMoO_3$$
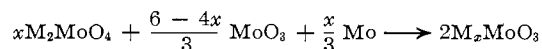
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