JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 80 SEPTEMBER 19, 1958 NUMBER 18

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION NO. 628 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Bismuth(I) Chloride[1]

BY JOHN D. CORBETT

RECEIVED MARCH 31, 1958

The reaction of $BiCl_3$ with excess bismuth below 323° results in the formation of solid BiCl. Although this three phase system is metastable, limited contact between the trichloride and metal phases apparently restricts the yield to about 75 mole % BiCl. That the product is the reported bismuth(I) chloride is confirmed by its isolation in 98 to 99% purity by sublimation or benzene extraction of the unreacted $BiCl_3$ from the BiCl–$BiCl_3$ mixtures. The monochloride's principal reaction is disproportionation; it decomposes to trichloride and metal phases at 323°. The black, diamagnetic material is rather stable in air at room temperature. Powder pattern data given in the literature for BiCl–$BiCl_3$ mixtures as well as for two forms of $BiCl_3$ are found to be primarily those for the products of reaction of $BiCl_3$ with atmospheric moisture. No evidence for a non-stoichiometric BiCl phase or for the existence of $BiCl_2$ is found. The apparent occurrence of the monochloride as $(BiCl)_n$ is discussed.

Introduction

There is considerable disagreement in the literature as to the identity of the lower chlorides, bromides and iodides of bismuth; the following discussion of the literature will be concerned primarily with the chlorides. Although the preparation of the black $BiCl_2$ had been claimed in a number of earlier references,[2] the first substantial characterization of the Bi–$BiCl_3$ system was presented by Eggink[3] in the form of a phase diagram. Apparent solution of metal in molten $BiCl_3$ was found to take place to a considerable extent. More significantly, when the two-liquid phase system obtained with excess metal was cooled, an intermediate solid phase separated at temperatures above the melting point of either component. Extraction of the excess trihalide from the solid salt mixture with ether gave a product analyzing very close to BiCl. The separation of BiBr by a similar treatment also was claimed; no properties were reported for either compound. It now appears that these results are qualitatively correct, although Eggink's conclusions regarding the existence of $BiCl_4$ have been questioned.[4]

At the same time Herz and Guttmann[5] concluded from thermal analysis that only the dihalide was stable in these systems. No explanation other than supercooling or gross impurities seems satisfactory for the excessively low temperatures observed. Aten[6] concluded that only ionic conduction was present in molten $BiCl_3$ containing dissolved metal.

Marino and Becarelli[7] reached somewhat different conclusions regarding these systems. Since the intermediate phase that separated did not show a constant composition, the systems were interpreted in terms of the formation of a continuous series of mixed crystals which melted higher than either component. In retrospect, it would be unusual if such a phase were to separate quantitatively from the adhering trihalide solution. Montignie[8] reported the preparation of $BiCl_2$ (and $BiBr_2$) by several means, most of which, as with some earlier workers,[2] predetermined the final composition by the use of an initial halide to bismuth ratio of two. Baroni[9] found only lines due to $BiBr_3$ in a powder pattern of the latter material.

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[1] Presented in part at the symposium on Unfamiliar Oxidation States of the Elements, 131st meeting of the American Chemical Society, Miami, Florida, April 10, 1957.

[2] Heintz, *Ann. Physik.*, [2] **63**, 59 (1844); R. Schneider, *ibid.*, **96**, 130 (1855); R. Weber, *ibid.*, **107**, 596 (1859); P. Muir, *J. Chem. Soc.*, **29**, 144 (1876).

[3] B. G. Eggink, *Z. physik. Chem.*, **64**, 449 (1908).

[4] L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, p. 251.

[5] H. Herz and A. Guttmann, *Z. anorg. Chem.*, **56**, 422 (1908).

[6] A. Aten, *Z. physik. Chem.*, **66**, 641 (1909).

[7] L. Marino and R. Becarelli, *Atti accad. Lincei*, **21**, 695 (1912); **24**, 625 (1915); **25**, 105, 171, 221, 326 (1916); AEC translations 2981, 2982, 2983, 2985, 3010, 2984, resp.

[8] E. Montignie, *Bull. soc. chim. France*, [5] **3**, 1083 (1936); **4**, 588 (1937).

[9] A. Baroni, *Atti accad. Lincei*, **25**, 195 (1937).

In 1949 Sokolova[10] redetermined the Bi–$BiCl_3$ phase diagram with the same general results as Eggink. From $BiCl_3$ to Bi her results, with those of Eggink in parentheses, are: eutectic at 28.5-(14.7) mole % Bi and 200(210)°; two liquids in equilibrium with solid phase from 60(41) to 97(94)% Bi at 318(320)°; eutectic at 97.5(98)% Bi and 265(267.5)°. The new phase was considered to be BiCl, corresponding to 66.7 mole % metal, although the compound was not isolated and the phase relationships actually allow rather wide limits for its composition. Unfortunately, the invariant nature of the three phase system at 318° apparently was not recognized. Equilibrium at such a syntectic point is often reached very slowly,[11] and this is reflected in the eutectic halts at lower temperatures. Solidification of the metal-rich phase was observed as far as 50% metal and that of the salt phase, to 80%, both with considerable (30 to 55°) supercooling. The last effect was attributed to decomposition of the BiCl. In addition, the negative temperature coefficient for the solubility of BiCl in $BiCl_3$ above 318°[12] made the composition of that phase rather uncertain when cooled from higher temperatures. In a later paper Sokolova and coworkers[13] also reported X-ray and microstructure observations. The presence of a new phase was detected by means of powder patterns in quenched but not in slowly cooled BiCl–$BiCl_3$ solutions; the BiCl was reported to disproportionate almost completely in 18 to 20 minutes at room temperature. A second crystalline form of $BiCl_3$ was found, and a BiCl isostructural with BiOCl was claimed on the basis of abnormal intensity distribution in a pattern similar to the latter. Similar results have been obtained for the bromide system.[14] Information in the literature on the bismuth iodides indicates that further work is necessary on a probable lower iodide.[4,15]

The extreme slowness with which equilibrium is attained between the two liquid phases and the solid subchloride has been noted by Holecek and Wilmarth,[16] and a powder pattern for the compound obtained from that of a BiCl–$BiCl_3$ mixture. Unpublished work on the Bi–$BiCl_3$ system has shown the consolute temperature for the two liquid phases is at about 778°[12]; also a phase has been separated which is "largely bismuth monochloride."[17]

It is fairly certain from the foregoing citations that the solution of metal in $BiCl_3$ is not solely a phenomenon of the liquid state but rather that a new phase is formed under certain conditions. Although the simplest interpretation is formation of the stoichiometric BiCl, there is no substantial report of its isolation and characterization. The present paper serves to report the separation of bismuth(I) chloride by two different methods and the determination of some of its physical and chemical properties.

Results and Discussion

Since the three phase system $BiCl_3$–BiCl–Bi is metastable below about 320°, equilibration of the trichloride with excess metal at lower temperatures should in principle result in complete reduction to BiCl; such an approach has been useful in the Ga–Ga_2Br_4 system where a syntectic relationship is found for GaBr.[18] However, even with agitation for several days at 310° the best product obtained corresponded to only about 78 mole % BiCl. Contact between the phases was apparently very poor, due at least in part to the intermediate density and porosity of the BiCl. Furthermore, the shaking occasionally resulted in distributed metal that could be identified and removed only after heating the powdered mixture to *ca.* 300°. The largest amount of BiCl that can be obtained in solution under reasonable conditions is at the syntectic temperature; direct determination of this value by filtration *in situ* at 338° gave 68 ± 1 mole % BiCl, as compared to reported values at 318, 320 and 325° of 57,[3] 90[10] and 67.5%,[12] respectively. The most convenient method for the preparation of mixtures that contain a maximum amount of the crystalline monochloride was found to be slow cooling of the above solution in the presence of excess metal from 325 to 270° over a period of one to three weeks; the yields are nearly as good (72 to 76%) as with agitation.[19]

Sublimation of the excess $BiCl_3$ from such a mixture is a suitable method for the isolation of BiCl. The black monochloride can be heated in an evacuated container for long periods at 180° and for several days at 190° without disproportionation. Decomposition in rather small amounts is evidenced by the appearance of the light gray metal as well as by X-ray examination. However, even though the vapor pressure of $BiCl_3$ is about 0.3 mm. at these temperatures,[4] the sample must be reground in the dry box several times during the separation. Typical results are shown in Table I.

TABLE I

SUBLIMATION OF $BiCl_3$ FROM BiCl *in vacuo*

Starting material, mole % BiCl	Sublimation	Product Wt. % Bi[a]	Mole % BiCl
68	3 da., 180°	84.92	97.7
97.7	1 da., 190°	85.03	98.1
ca. 75	11 da., 160°[b]	84.32	95.2
95.2	3 da., 178°[b]	85.07	98.3

[a] BiCl is 85.496 wt. % Bi. [b] Larger samples, two intermediate grindings.

Progress of the sublimation is best followed by intermediate analysis; a leveling off in the amount

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(10) T. I. Sokolova, *Isvest. Sektora Fiz-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk SSSR*, **21**, 159 (1952?); *AEC translation* No. 3168.

(11) F. R. Rhines, "Phase Diagrams in Metallurgy," McGraw-Hill Book Co., New York, N. Y., 1956, Chapter 10.

(12) S. Yosim, A. Darnell and W. Gehman, Abstracts of Papers, ACS Meeting, New York, N. Y., Sept. 1957, p. 8-N.

(13) M. A. Sokolova, G. G. Urazov and V. G. Kuznetsov, *Khim. Redkikh Elementou, Inst. Obshchei Neorg. Khim., Akad. Nauk SSSR*, **1**, 102 (1954).

(14) G. Urazov and M. A. Sokolova, *Isvest. Sektora Fiz-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk SSSR*, **24**, 152 (1953?).

(15) G. Urazov and M. A. Sokolova, *ibid.*, **25**, 117 (1954).

(16) O. C. Holecek, "Physical-Chemical Investigation of the System Bi–$BiCl_3$," Thesis, Univ. So. Calif., Los Angeles, Calif., 1953; W. K. Wilmarth, private communication.

(17) S. Mayer, S. Yosim and A. Darnell, Abstracts of Papers, ACS Meeting, New York, N. Y., Sept. 1957, p. 28-S.

(18) J. D. Corbett and A. Hershaft, THIS JOURNAL, **80**, 1530 (1958).

(19) Similar results have been obtained with BiBr.

of trichloride removed as the composition approaches BiCl is then quite apparent. Metal was not detected in powder patterns of the final products.

Although solvent extraction of the excess $BiCl_3$ offers obvious advantages, disproportionation of the monochloride results in many instances. At room temperature acetonitrile, dimethylformamide, water and hydrochloric acid all cause decomposition in rather short time, while dioxane apparently forms an insoluble complex with $BiCl_3$. Diethyl ether also causes some (7–45%) disproportionation during the time (24 hr.) necessary to remove the majority of the $BiCl_3$, as indicated both by analysis and by powder patterns. Bismuth oxychloride is also produced by the traces of water that are present in ether that has even been stored and refluxed over calcium hydride. It therefore appears unlikely that Eggink[3] succeeded in the isolation of very pure BiCl in this manner.

Benzene that has been distilled from lithium aluminum hydride gives the best results, as shown in Table II.[20] But even with this solvent excessive extraction causes some disproportionation; a composition of 86.8 wt. % bismuth resulted from more rapid extraction for 36 hours of a small sample that initially contained 83.1 wt. %. Powder patterns of the last two products show a few faint lines due to free metal; these disappeared after heating for one week at 310° due to reaction of the metal with the small excess of trichloride. The much higher crystal symmetry of bismuth metal makes this a relatively sensitive test. The extraction could well be repeated after this treatment for a product of higher purity. Without this the separation of BiCl by benzene extraction is probably not as good as by sublimation, although it is considerably faster.

TABLE II

SOXHLET EXTRACTION OF $BiCl_3$ FROM BiCl WITH BENZENE

Starting material, % BiCl	Extraction time, hr.	Product Wt. % Bi[a]	Product Mole % BiCl
76	37	84.81	97.2
97.2	8	85.06	98.2
76[b]	29	85.03	98.1
76[b]	34[c]	85.23	98.9

[a] BiCl is 85.496 wt. % Bi. [b] Ground particularly fine. [c] One intermediate grinding.

Even though non-stoichiometric halide phases are now known only for the transition metals,[21] some consideration has been given to this possibility. The preceding data as well as an invariance in the powder pattern spacings of BiCl for mixtures containing either $BiCl_3$ or Bi seem to rule out a significant variation in composition. A mixture of BiCl and finely powdered metal can be heated for two weeks at 250 to 310° without effect on their patterns. On this basis it is concluded that the intermediate phase in the Bi–$BiCl_3$ system is within 1% of the stoichiometric bismuth(I) chloride. Certainly the phase diagram shows no indication of $BiCl_2$; furthermore, no evidence for its existence is found in the powder pattern of a mixture of that composition that has been cooled from 190° to room temperature over a period of 10 days.

No suitable solvent has been found for BiCl other than $BiCl_3$, where the disproportionation is naturally repressed. The compound reduces $SbCl_3$ and does not dissolve in $AsCl_3$. It does react with molten $AlCl_3$ to form the previously reported $Bi(AlCl_4)$,[22] which in turn has a limited solubility in $AlCl_3$ but dissolves excess BiCl to a small extent. As expected, BiCl decomposes to two liquids at the syntectic temperature, 322 and 324 (±0.5)° being observed for two different preparations.

The powder pattern data obtained for BiCl (experimental section) agree quite well with those deduced by Holecek[16] from mixtures of BiCl and $BiCl_3$ but bear little resemblence to those reported by Sokolova, *et al.*[13] Moreover, it has not been possible to confirm the existence of a second crystalline form of $BiCl_3$ that was reportedly observed when powder pattern capillaries were filled directly from the molten salt.[13] The same pattern is obtained for $BiCl_3$ that has been either sublimed, annealed one week at 210° and then quenched, cooled slowly or quenched from 250° or sucked molten into capillaries. The most likely explanation for these discrepancies is the presence of hydration and hydrolysis products of at least the $BiCl_3$ in the samples examined, as evidenced by their detection of BiOCl in BiCl–$BiCl_3$ mixtures. Certainly BiOCl is not the immediate hydrolysis product of $BiCl_3$ at room temperature, as HCl is seldom detected. It has been found that one or more new phases appear in patterns taken of vacuum-sublimed trichloride that has been exposed to the atmosphere for three minutes; these as well as BiOCl and other products are also found with commercial "C.P." $BiCl_3$. One-half of the distances >1.3 Å. reported for the new form of $BiCl_3$ can be attributed to those observed in this fashion, while the remainder appear to be those of the trichloride. Better than 75% of the distances >1.3 Å. in the pattern cited as normal $BiCl_3$ appear to be due to these impurities, while those for BiCl are about equally distributed among BiCl, the above impurities and unidentified lines. In contrast, the data given for bismuth metal agree well with those found in this work. It appears that the reported X-ray data for the bromide[14] and iodide[15] systems should be treated with some reservation.

Shiny, black crystals of BiCl in the form of long rods with elongated-hexagonal cross-section can be grown from the saturated BiCl–$BiCl_3$ melt with slow cooling. These are also found extending out of the three phase system after prolonged equilibration at 310°. In contrast to the effect of liquid water the crystals are quite stable to atmospheric moisture, and only light surface decomposition is noticed after several weeks. Preliminary X-ray examination shows these to be of orthorhombic symmetry, with a unit cell of about 23 × 15 × 8 Å. From an experimentally determined density of 6.95 g. cc.$^{-1}$, Z is about 50.

On the basis of other observations it appears likely that BiCl is polymerized in some manner. The compound is diamagnetic, as are $Bi(AlCl_4)$[22]

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[20] The solubility of $BiCl_3$ in benzene is 0.287 wt. % at 26°.

[21] H. Schafer, *Angew. Chem.*, **67**, 748 (1955).

[22] J. D. Corbett and R. K. McMullan, THIS JOURNAL, **78**, 2906 (1956).

and solutions of BiCl in $BiCl_3$,[16,23] whereas Bi(I) would be expected to have two unpaired electrons. One possible explanation is that polymerization occurs through the formation of bismuth–bismuth bonds. A cyclic unit appears more likely since open chain units would be inconsistent with the diamagnetism and the following observation on the degree of polymerization.

The $BiCl_3$–BiCl portion of the phase diagram at first appears somewhat unusual, since the eutectic corresponds to about 43 mole % BiCl and is less than 40° below the melting point of the trichloride. If values of N_{BiCl_3} are calculated on the basis of various values of n for the solute $(BiCl)_n$, some indication of n can be obtained from a comparison of plots of log N_{BiCl_3} *vs.* $1/T$ with the theoretical line corresponding to the known heat of fusion of $BiCl_3$.[4] Using smoothed values of the temperatures reported,[10] it appears that n is equal to 4, the fit in this case being very good for the first half of the range. Values of 5 and 6 extrapolate to the correct slope fairly well but require negative deviations approaching the formation of $(BiCl \cdot BiCl_3)_n$ even in fairly dilute solution. Remarkably ideal solutions have been found in a similar treatment of the Cd–$CdCl_2$ system.[24] The data for an n of three appear less satisfactory, the apparent heat of fusion being too high. However, the original data are probably not good enough to rule out the trimer, since they involve a scatter up to 2°, a surprisingly high melting point for $BiCl_3$ (240°) and apparently some supercooling near the eutectic. Unpublished cryoscopic studies by Yosim and co-workers[17] are doubtless more accurate and reportedly indicate a trimer. An increase in viscosity has been noted when BiCl is formed in liquid $BiCl_3$.[6,10]

Experimental

For the initial work J. T. Baker reagent grade bismuth was freed of non-metallic impurities by vacuum fusion, manual and acid cleaning and fusion with KCN. For the final products reported herein a 99.999% A. D. MacKay product was used. Commercial $BiCl_3$ that has been vacuum sublimed has a light brown to gray color as a solid and is very dark when fused. The color apparently is due to an organic impurity as it can be removed by sublimation in a chlorine atmosphere. However, because of the apparent volatility of oxygen-containing compounds, as noted before,[16] the trichloride usually was prepared from metal and dry chlorine. The vacuum sublimed product was stored in fragile ampoules and subsequently handled as previously described.[23]

Sublimation of $BiCl_3$ from BiCl was carried out in 12 mm. tubing that had been sealed off under diffusion-pump vacuum after being heated to 150–170°. Position-proportioning temperature control was used as off-on control gave sufficient overheating to cause decomposition. Samples were periodically ground in the dry box and portions taken for analysis. Benzene extractions were performed in conventional Soxhlet apparatus lubricated with silicone grease and under a positive pressure of dry argon. Benzene was distilled from $LiAlH_4$ into the pot after having been stored over CaH_2. Some indication of the generation of BiH_3 was noted when the hydride was present during the extraction. The extraction thimbles (Whatman, fat-free) were washed and vacuum-dried before being filled with the powdered samples in the dry box. Acetonitrile, DMF and dioxane were vacuum-distilled from CaH_2, and $AsCl_3$, from arsenic.

Samples taken in the dry box for analysis were placed in lightly greased weighing bottles and the sample weight determined by difference, corrected for the buoyancy of helium in the box. The final products shown in Tables I and II could be weighed in air without any detectable change; in addition, they did not give the immediate milkiness with water that is characteristic of $BiCl_3$. They were dissolved in 3 N HNO_3 and the bismuth determined by the thiourea–Versene method of Fritz.[25] In order to avoid thiourea decomposition due to the high acid concentration, 7 N NH_4OH was added to aliquots until a permanent precipitate formed before the indicator was added. Versene solutions were standardized against solutions prepared by the solution of bismuth metal in HNO_3. The titrations were reproducible to 0.005 ml. Analyses of $BiCl_3$ samples prepared as above were within 0.1 wt. % Bi of the theoretical value, most of the variation being due to a 1 mg. variation in the buoyancy correction for which allowance was not made.

In view of the sources and care used in the preparation of BiCl, there is ample reason to believe that chloride and bismuth are the only materials present in the samples in appreciable amounts. This was confirmed in a few cases by precipitation of the chloride as AgCl. For example, the next to the last sample in Table II analyzed 99.94 ± 0.07 wt. % Bi plus Cl; the error assigned is the maximum due only to the uncertainty in reading the buret and the balance.

Powder pattern data were obtained as previously described.[18] Due to the high absorption and relatively low crystal symmetry of BiCl, Pyrex capillaries not greater than 0.15 mm. i.d. were necessary to obtain satisfactory data. The high background density at large scattering angles was also indicative of the high sample absorbency. The following distances, in ångströms, with relative intensities in parentheses, correspond to the principal lines observed for BiCl: 8.99(3), 3.91(10), 3.76(8), 3.39(5), 2.91(8), 2.88(8), 2.79(4), 2.65(10), 2.52(5), 2.42(3), 2.393(5), 2.286(4), 2.220(7). 2.093(5), 2.036(3), 2.016(3), 1.527(4); 21 weaker lines were also observed. For $BiCl_3$ the data are 4.79(10), 3.30(9), 2.91(9), 2.75(4), 2.58(9), 2.27(10), 2.14(4), 2.09(4), 2.06(4), 1.960(4), 1.864(9), 1.842(9), 1.660(5), 1.463(5), 1.437(5), 1.334(5), 1.321(5), 1.218(4), 1.170(4), 1.154(4), 1.145(4); 38 weaker lines also were observed. The strongest new lines observed when $BiCl_3$ is briefly exposed to the atmosphere correspond to the distances 5.50, 5.27, 4.53, 4.34, 3.42, 3.36, 3.13, 2.81, 2.67, 2.54, 2.37, 2.34, 2.14, 1.966, 1.711. The spacings observed between 2 and 3 Å. varied an average of less than 0.007 Å. from $BiCl_3$- to Bi-rich samples of BiCl. No solid solution of BiCl in $BiCl_3$ could be detected. The strongest Bi reflection (102) observed at 3.27 Å. is the most convenient for its identification. The density of BiCl was measured with a pycnometer using dry benzene as the known liquid, and was corrected for the $BiCl_3$ content indicated by analysis, using a density of 4.75 g. cc.$^{-1}$ for $BiCl_3$.

Acknowledgments.—Appreciation is expressed to Alex Hershaft for the single crystal X-ray studies of BiCl and for translations of references 10 and 14 and to Drs. Dan Cubicciotti and Sam Yosim for copies of translations of references 7 and 13, respectively.

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(25) J. S. Fritz, *Anal. Chem.*, **26**, 1978 (1954).