[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASHINGTON]

Preparation and Reactions of Potassium Silyl[1]

BY M. A. RING AND D. M. RITTER

Potassium silyl was isolated as cubic crystals from its solution in 1,2-dimethoxyethane, where it was prepared by the reaction of silane and potassium, with hydrogen and potassium hydride as the other products. It was formed also when potassium and disilane reacted, and there was found between potassium hydride and disilane an equilibrium reaction so far displaced toward formation of potassium silyl and silane that isotope exchange was required to demonstrate the reverse reaction. The substance reacted with water, hydrogen chloride and methyl chloride and decomposed in a vacuum at 240°, all quantitatively. Reaction was observed also with bromosilane, silicon tetrabromide and with diborane.

Introduction

Many years ago, following an earlier preparation of sodium germyl,[2] Sampson Isenberg[3] and W. C. Johnson observed the rapid reaction of potassium metal with silane in liquid ammonia to give a white crystalline product from which silane was regenerated by the action of ammonium cations, and methyl silane was obtained by reaction with methyl chloride. There is little doubt that those properties belonged to potassium silyl,[4] but ammonolysis prevented isolation of the substance. Recently similar reactions with stannane and dimethyl stannane have been observed through conductimetric titration in liquid ammonia.[5]

This paper concerns the isolation and identification of potassium silyl as the product from the reaction of silane or disilane in the aprotic, therefore non-solvolytic, solvent for the product and for potassium, 1,2-dimethoxethane.[6,7] In addition some chemical reactions of the substance have been observed.

Experimental

General Experimental Methods.—The manipulative methods were those in general use for work in high vacuum.[8,9]

The substances prepared or purified by known methods or obvious adaptation of these were silane,[10] disilane,[11] potassium hydride[12] and potassium deuteride,[12] silicon

tetrabromide,[13] potassium,[14] sodium–potassium alloy,[15] trideuteriobromosilane.[16]

The largest of several reaction vessels for preparation of potassium silyl was constructed from a 30 cm. X 8 cm. dia. Pyrex glass cylinder closed hemispherically at one end and at the other fitted with a tube 2 cm. dia. X 8–10 cm. long. This latter had a medium porosity sintered glass filter across the mid-point, perpendicular to the axis, and beyond the filter was a fragile bulb-impact-fracture closure constructed from 1 cm. tubing. Sealed to the 2 cm. tube on the cylinder side of the filter was a 1 cm. tube, serving as a manifold leading to entry and exit tubes for pumping, introduction of reagents and removal of products.

Preparation and Isolation.—1. Potassium (about 2 g.), introduced by distillation, monoglyme (10–15 ml.) and silane (about 50 mmole) were condensed in an evacuated vessel, which was then sealed from the vacuum apparatus. The bottom half of the vessel was immersed in a Dry Ice–acetone bath (−78.5°), shaken gently every few days and kept there for 2 months. Next the hydrogen was measured, and the solution was filtered into the receiver, which was fitted with closures to permit later transfer operations. In one experiment of 14 days duration, using sodium–potassium alloy, 46.1 mmole of silane was consumed and 3.90 mmole hydrogen produced. Where potassium metal was the reactant, experiments lasted 60,70,74 and 76 days; silane was consumed in the amounts of 30.0, 48.2 57.1 and 5.30 mmole, respectively, corresponding to 75% consumption in the first and fourth experiments and complete use in the other two. The hydrogen produced was 12.0, 6.57, 25.8 and 1.59 mmole, respectively.

2. (a) When disilane was used instead of silane at −78.5° potassium (5 g.), monoglyme (40 ml.) and disilane (32.9 mmole) were stored for 2 months. The volatile substances found were silane (8.65 mmole) and hydrogen (2.0 mmole). Treatment of a portion of the solute with hydrogen chloride gave silane (3.1 mmole) and disilane (0.26 mmole). Another portion, treated with methyl chloride, gave methyl silane (2.02 mmole), silane (0.55 mmole) and disilane (0.1 mmole).

(b) Potassium (0.5325 g.), disilane (1.00 mmole) and monoglyme (5 ml.) were stored at room temperature. After 2.5 hr., 0.23 mmole of disilane was recovered and silane (0.93 mmole) appeared as the volatile product. Treatment of the solute with excess methyl chloride gave methyl silane (0.25 mole) and an undetermined quantity of silane. Specific examination of the infrared spectra for evidence of dimethyl silane[17] revealed none.

3. (a) Where potassium hydride was used, an excess was treated with disilane (3.28 mmole) and monoglyme (4 ml.) at room temperature. After one day the disilane was consumed, and 3.14 mmoles of silane had appeared.

(b) Similarly disilane (2.88 mmole) and monoglyme (3 ml.) were condensed on lithium hydride (15.8 mg.) A white solid deposited during the 48 hr. reaction time; there-

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1541. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Charles A. Kraus and E. Seaton Carney, THIS JOURNAL, 56, 765 (1934).

(3) Sampson Isenberg, Doctoral Dissertation, University of Chicago (1937).

(4) The name for this substance in chemical abstracts usage is potassium trihydridosilicon, cf. ref. 2; however IUPAC nomenclature for organometallic compounds endorses "dimethylzinc" which for ionic substances becomes "sodium methyl." Thus by analogy the name potassium silyl can be deduced.

(5) H. J. Emeleus and S. F. A. Kettle, J. Chem. Soc., 244 (1958); S. F. A. Kettle, ibid., 2936 (1959).

(6) The fact that polyethers are solvents for potassium was communicated privately by Prof. S. I. Weissman, Washington University, St. Louis in June, 1956, as the result of observations made in collaboration with T. R. Tuttle, Jr.; cf. J. L. Down, J. Lewis, B. Moore and G. Wilkinson, Proc. Chem. Soc., 209 (1957).

(7) Eastman Chemical No. 472 commonly called monoglyme.

(8) As developed by Alfred Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, and by H. I. Schlesinger and his co-workers, described by R. T. Sanderson "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(9) For vacuum transfer of fluids see S. G. Gibbins, Thesis, University of Washington, 1955, p. 31.

(10) A. E. Finholt, A. C. Bond and H. I. Schlesinger, THIS JOURNAL, 69, 1199 (1947).

(11) A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, ibid., 69, 2692 (1947).

(12) Henry Gilman, A. C. Jacoby and H. Ludeman, ibid., 60, 2336 (1938).

(13) Walter C. Schumb, "Inorganic Syntheses," McGraw–Hill Book Co., New York, N. Y., 1946, p. 99.

(14) G. W. Watt and D. M. Sowards, THIS JOURNAL, 76, 4742 (1954).

(15) J. F. Birmingham, Ind. Eng. Chem. Anal. Ed., 7, 53 (1935).

(16) Alfred Stock and Carl Somieski, Ber., 51, 989 (1918).

(17) Samuel Kaye and Stanley Tannenbaum, J. Org. Chem., 18, 1750 (1953).

after silane (0.5 mmole) and disilane (2.25 mmole) were recovered, and the solid was extracted into another vessel attached through a filter.

4. A solution of potassium silyl in monoglyme (about 20 ml.), obtained as described in experiments 1 or 3a, was kept at room temperature in one arm of an inverted U-shaped vessel with the second arm immersed in an ice bath. After a week, clear cube-shaped crystals appeared. The distillation was continued until only 2–3 ml. of solvent remained. After this mother liquor was decanted, more solvent was distilled on the crystals; these were re-dissolved and the procedure was repeated. Finally the vessel was opened in an anaerobic dry box.

No effort was made to determine the yields of potassium silyl directly because the nature of the crystallization precluded an easy recovery of all the product. The reactions in cases such as experiments 3 and 11 were essentially quantitative.

Reactions. 5. Hydrolysis–Analysis.—The crystals from experiment 4 were tumbled gently on an unglazed porcelain dish and after three minutes the drying appeared complete. Sample #1 (36.0 mg.) was then taken for weighing and transfer to the hydrolysis tube. Sample #2 (30.1 mg.) was permitted to remain on the porous plate for 1 hr. before it was weighed and transferred. The samples were contained in micro-scale platinum boats, which were kept in ground stoppered pigs for weighing. Water was condensed in the tubes at $-80°$, and the hydrolysis was permitted to continue for twenty minutes at room temperature. The calculated quantities should be: H 2.62%, Si 24.4%, K 33.8%, for $KSiH_3$; $1/2$ $C_4H_{10}O_2$, and H 4.31%, Si 40.0% and K 55.6% for $KSiH_3$. (a) Hydrogen was determined as hydrogen gas: found #1, 1.28 mole H_2, 0.97 mmole combined H or 2.70%; #2, 1.70 mmole H_2, 1.28 mmole combined H or 4.30%. (b) Silicon was determined spectrophotometrically[18]: found #1, 0.328 mmole Si or 24.4%; #2, 0.432 mmole Si or 40.3%. (c) Potassium was determined using the flame photometer attachment for a Beckman DU spectrophotometer.[19] Found #1, 0.316 mmole K or 33.8%; #2, 0.426 mmole K or 55.2%.

6. Treatment with Hydrogen Chloride.—Potassium silyl crystals (0.463 mmole) were treated with excess dry hydrogen chloride for 5 hr. at room temperature. The mixture of unused hydrogen chloride and silane was measured and then hydrolysed with aqueous potassium hydroxide solution to determine the silane. The hydrogen chloride consumed was 0.470 mmole. The products were silane (0.460 mmole) and potassium chloride (0.466 mmole). When 2 ml. of 4 N hydrochloric acid was mixed with a small volume of potassium silyl solution in monoglyme, hydrogen (1.06 mmole) and silane (0.4 mmole) were formed.

7. Reaction with Methyl Chloride.—In the same manner as with hydrogen chloride excess methyl chloride was condensed on potassium silyl (0.430 mmole). The gas mixture remaining was fractionated by successive passes through a trap cooled to $-130°$ until the infrared spectra showed that separation was complete into methylsilane (0.432 mmole) and residual reagent. The methyl chloride consumed was 0.432 mmole, and 0.434 mmole of potassium chloride was formed.

8. Thermal Decomposition.—Two crystals of potassium silyl, (0.268 mmole) were heated in vacuo. During a half hour from 80° to 230°, 0.012 mmole of hydrogen appeared. Above 240° the solid decomposed rapidly; the total hydrogen was 0.407 mmoles.

9. Reactions with Silicon Halides.—With the expectation of obtaining 1,1,1 trideuterodisilane, trideuterobromosilane (4.4 mmole) was added to slightly less than an equimolar quantity of potassium silyl in monoglyme.[20] A white solid formed (presumably potassium bromide), and after a day there remained a mixture of deuterosilanes (2.1 mmole), deuterodisilanes (0.085 mmole) and partially protonated deuterobromosilane (1.9 mmole).

Silicon tetrabromide reacted with a solution of potassium silyl in monoglyme in a somewhat similar way. Silane was the only volatile product; bromide ion was found in the

solid residue, which also gave strong infrared absorption at 3000 and 2170 cm.$^{-1}$ indicating C–H and Si–H bonds, respectively.

10. Reaction with Diborane.—Solid potassium silyl (3.18 mmole) was dissolved in monoglyme (2 ml.) and diborane (3.91 mmole) was condensed in the vessel. While the mixture stood at room temperature for 2 hr., a white solid formed. Then the gases more volatile than the solvent were separated; the components were identified by an infrared spectrum,[21] and the amounts were determined by hydrolysis in acid solution as 2.06 mmole diborane and 0.14 mmole silane. The solution was filtered and concentrated by evaporation, whereupon more solid and silane (0.40 mmole) formed. The solid was identified by analysis and by an X-ray powder pattern[22] as potassium borohydride: found, K, 71.1%; B, 19.5%; H, 7.64%; calcd., 72.5%, 20.1%, 7.46%, respectively.

The final amount of solvent was removed leaving a nonvolatile oil which could have contained residual monoglyme. Alkaline hydrolysis of the oil gave 5.17 mmoles hydrogen, and the resulting solution contained 1.08 mmoles of boron and 2.56 mmoles of silicon, determined as previously described.

Nature of the Reaction between Potassium and Silane.—
11. Potassium (6.98 mmole) was treated with excess silane. In the process 5.30 mmole of silane was consumed and 1.59 mmole of hydrogen formed. The solution was filtered to remove the solvent and as much potassium silyl as possible. Then the content of the reactor was treated with hydrogen chloride (6.84 mmole).[23] The volatile substances recovered were excess hydrogen chloride (2.97 mmole), hydrogen (1.95 mmole) and silane (1.81 mmole). The material balances were: for displaced hydrogen, 1.95 mmole as potassium hydride and 2×1.59 mmole as hydrogen gas, total 5.13 mmole compared with 5.30 mmole entering as silane; for hydrogen chloride, 1.81 mmole consumed by potassium silyl and 1.95 mmole consumed by potassium hydride, total 3.76 mmole compared with 3.87 mmole found from direct measurement; for potassium, found as potassium hydride 1.95 mmole, calculated from the hydrogen balance to be present as potassium silyl 5.13 mmole, a total of 7.08 mmole compared with 6.98 mmole added as the metal.

Reaction between Silane and Potassium Silyl Revealed by Isotope Exchange.—The relative abundances of deuterosilanes, produced in each of the exchanges, were estimated from intensities of known infrared bands.[24,25] Owing to inherent uncertainties only qualitative estimates of amounts of isotopic species were attempted, except in experiment 14 where exactly the same gas sample was observed before and after exchange.

12. When potassium hydride in excess was treated with tetradeuterosilane (1.18 mmole), the silane was recovered unchanged.

13. Disilane (3.28 mmole) and monoglyme (4 ml.) were condensed on potassium deuteride (4.62 mmole). After 48 hr. the mixture of deuterosilanes (3.04 mmole) contained $SiH_3D \cong SiH_2D_2 \gg SiH_4$; others were absent. The solution containing potassium silyl was filtered without attempting a quantitative recovery of solute. It was then treated with dry hydrogen chloride. The volatile product was deuterosilanes (1.05 mmole) with the same isotopic composition as the silanes produced directly from the disilane.

14. (a) Tetradeuterosilane (1.30 mmole) was condensed in a monoglyme solution of potassium silyl. After 24 hr. the mixture of deuterosilanes recovered (1.26 mmole) contained relatively 50 volume % tetradeuterosilane and 25 volume % each of trideuterosilane and dideuterosilane.

(b) Potassium hydride was suspended in a monoglyme solution of potassium silyl, and tetradeuterosilane (0.62

(18) Michael A. Resesa and Lockhart B. Rogers, Anal. Chem., 26, 1278 (1954).

(19) H. H. Willard, L. L. Merrill and J. A. Dean "Instrumental Methods of Analysis." D. Van Nostrand, New York, N. Y., 1951. p. 39.

(20) The experiments with trideuterobromosilane were performed by Mr. R. E. Wilde.

(21) For diborane: Am. Petroleum Inst. Project 44 IR Spectral Data, Serial No. 742 (1948–1949). For silane: W. B. Steward and H. H. Nielsen, Phys. Rev., 47, 828 (1935).

(22) S. C. Abrahams and J. J. Kalnis, J. Chem. Phys., 22, 434 (1954).

(23) Potassium metal will not react with hydrogen chloride at 25°; potassium hydride gives hydrogen; cf. Gmelins Handbuch der anorg. chem. Teil 22, Kalium, p. 169; Teil 6. Chlor, p. 128.

(24) Perkin–Elmer Model 21 infrared spectrometer with sodium chloride optics.

(25) Janet Hawkins Meal and M. Kent Wilson, J. Chem. Phys., 24, 385 (1956); monodeuterosilane[10,11] had bands at 2174, 1592, 953, 929, 908. 781 cm.$^{-1}$.

mmole) was added. After 48 hr. the deuterosilane mixture (0.59 mmole) was removed; the solution was separated by filtering and the solid on the filter and in the vessel was well-washed to remove all the potassium silyl. The solvent was finally restored to the reaction vessel, and the vessel containing potassium silyl was removed by sealing. Thereafter the solid residue (potentially a mixture of potassium hydride and potassium deuteride) suspended in the monoglyme was treated with disilane (0.85 mmole). A mixture of deuterosilanes (0.82 mmole) was obtained having the relative composition $SiH_3D \cong SiH_2D_2$.
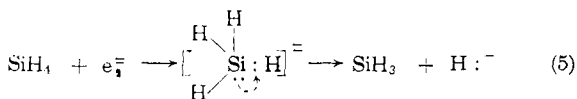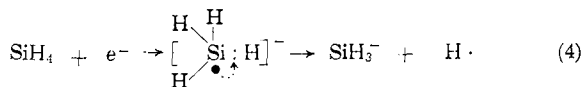
15. Finely powdered lithium deuteride was transferred to a reaction vessel in the dry-box. Disilane (1.03 mmole) and monoglyme (4. ml.) were condensed into the vessel. The deuterosilane mixture (1.03 mmole) found after 72 hr. had the relative composition $SiH_3D > SiH_4 >> SiH_2D_2$.

Results and Discussion

A solution of potassium silyl in monoglyme[7] was prepared: (A) from silane and potassium or sodium-potassium alloy, or (B) from disilane and potassium hydride. Filtered solutions from the preparative steps varied from colorless to yellow or green. Slow removal of the solvent produced clear, colorless cube-shaped crystals. The crystal structure, determined by X-ray powder analysis, is cubic of the sodium chloride type with $a_0 = 7.15 \pm 0.02$ Å.,[26] which suggests a salt-like character.

Potassium silyl reacted with water, gaseous hydrogen chloride, methyl chloride, and it decomposed at 240°. All these reactions were quantitative, permitting their use for analysis. The substance also reacted with bromosilane and with diborane in less precisely defined fashion. The cation appeared to affect reactivity, as has been observed for alkali metal methyls; thus the lithium compound reacted slowly with water and not at all with dry hydrogen chloride.

When the Group IV hydrides reacted with alkali metal in liquid ammonia, there was formed an equivalent yield of hydrogen,[2,3,5] but when silane reacted with potassium in monoglyme, a variable proportion of hydrogen was observed, always less than one equivalent. Hydrogen removed from silicon but not appearing as hydrogen gas was retained in the condensed phase as potassium hydride, as demonstrated in experiment 11. Both products can be accounted for by assuming an assuming an attack on the silane by the components of the metal solution to form an sp^3d transition state. Whether the metal solute model considered be that for the "electron-in-cavity" or the one for the "expanded orbital",[27] the dimer species should give hydride anion and the monomer should produce molecular hydrogen, with the silyl derivative formed in either case, as illustrated by the equations

$$SiH_4 + e^- \rightarrow \left[\begin{matrix} H & H \\ & \diagdown | \\ & Si \because H \\ & \diagup \\ H & \end{matrix} \right]^- \rightarrow SiH_3^- + H \cdot \quad (4)$$

$$SiH_4 + e_2^= \rightarrow \left[\begin{matrix} H & H \\ & \diagdown | \\ & Si \because H \\ & \diagup \\ H & \end{matrix} \right]^= \rightarrow SiH_3^- + H :^- \quad (5)$$

The reaction of potassium with disilane must be more complex than that with silane. Certainly it is no simple cleavage of the silicon–silicon bond.
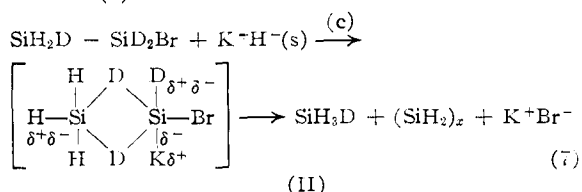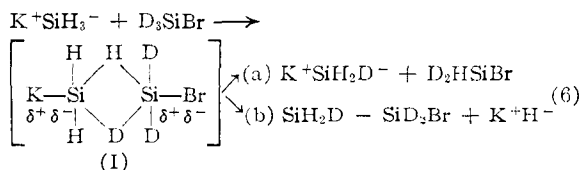
(26) M. A. Ring and D. M. Ritter, J. Phys. Chem., 65, 182 (1961).
(27) M. C. R. Symons, Quart. Rev., 13, 99 (1959).

Potassium silyl and a smaller amount of potassium disilanyl are products, logically so, but how so much silane forms is puzzling. Any explanation requires multiple reaction schemes for which too few facts are available as support.

No products could be found and the reagents were recovered quantitatively when silane was treated with potassium silyl, but, considering the number of nucleophilic reagents which remove hydride ion from the silanes,[28] a reaction would be thought plausible were there not known the reverse reaction of potassium hydride with disilane. To test for reversibility a deuterium-hydrogen exchange scheme was devised. The exchanges examined were experiments: (12) potassium hydride and tetradeuterosilane, (13) potassium deuteride and disilane, (14) potassium silyl and tetradeuterosilane (a) without a reservoir of potassium hydride and (b) with such a reservoir, and (15) lithium deuteride and disilane. When no exchange was found in (12), potassium hydride and potassium silyl were also assumed not to exchange. Without exchange in (13) the products should have been potassium silyl and monodeuterosilane. In (14 a, b) the possible exchange routes were through formation of potassium deuteride and deuterated disilane or directly without such a reaction. In (14 b) the potassium hydride reservoir was found to contain potassium deuteride at the end of the experiment, and correspondingly the silanes were enriched in hydrogen compared with the deuterated silanes recovered from (14 a). Thus, whatever other exchange paths were available, one of them led to formation of potassium deuteride and deuterated disilane from potassium silyl and tetradeuterosilane.

The reaction of potassium silyl with deuterobromosilane appears closely related to that with silane. Only about 4% of the expected 1,1,1-trideuterodisilane appeared. Instead, an approximately equivalent quantity of deuterated silanes was obtained; the excess deuterobromosilane became protonated, and from the material balance it could be concluded that, while potassium silyl had been transformed, an equivalent quantity of silicon still remained in the condensed phase. Bridge-bonded sp^3d transition states (I) and (II) can account for the products

$$K^+SiH_3^- + D_3SiBr \rightarrow$$

$$\left[\begin{matrix} H & H & D \\ & | \diagup \diagdown & | \\ K-Si & & Si-Br \\ \delta^+ \delta^- | \diagdown & \diagup | \delta^+ \delta^- \\ H & D & D \end{matrix} \right] \begin{matrix} \nearrow(a) \; K^+SiH_2D^- + D_2HSiBr \\ \\ \searrow (b) \; SiH_2D - SiD_2Br + K^+H^- \end{matrix} \quad (6)$$

(I)

$$SiH_2D - SiD_2Br + K^-H^-(s) \xrightarrow{(c)}$$

$$\left[\begin{matrix} H & D & D_{\delta^+ \delta^-} \\ & | \diagup \diagdown & | \\ H-Si & & Si-Br \\ \delta^+ \delta^- | \diagdown & \diagup | \delta^- \\ H & D & K\delta^+ \end{matrix} \right] \rightarrow SiH_3D + (SiH_2)_x + K^+Br^- \quad (7)$$

(II)

(28) Lithium methyl: H. Gilman and S. P. Massie, This Journal, 68, 1880 (1946); H. Gilman and H. W. Melvin, ibid., 71, 4050 (1949); lithium ethyl: J. S. Peake, W. H. Nebergall and T. C. Yun, ibid., 74, 1526 (1952); sodium triethylzincate: S. G. Gibbins, ref. 9, p. 11; hydroxyl ion: F. P. Price, ibid., 69, 2600 (1947).

Path a is the non-symmetrical withdrawal from the transition state; path b is the disilane + potassium hydride formation previously diagnosed and path c is the normal reaction of potassium hydride and a disilane derivative. In addition to bridge bond formation dipole orientation can contribute to determining the structures of particular transition states. Formation and withdrawal along path a from a transition state such as (I) can constitute a route for direct isotopic exchange in experiments 13 and 14 a,b, while along path b the same transi- tion state can give exchange *via* potassium hydride formation.

As a base silyl anion should form a 1:1 adduct with borane, BH_3, acting as a generalized acid. The proportions observed were 1:1.16, but the adduct anion was unstable, undergoing disproportionation with respect to boron to produce borohydride anion and with respect to silicon to produce silane. The other product appears to be one or more probably condensed species, which will be characterized later.

[Contribution from the Department of Chemistry and the Lawrence Radiation Laboratory of the University of California, Berkeley, California]

The Oxidation States of Astatine in Aqueous Solution[1]

By Evan H. Appelman[2]

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The redox equilibria among the oxidation states of astatine have been studied in acidic solution. Reversible couples have been used and equilibria have been approached from both sides. The −1, 0, +1 (?) and +5 states have been characterized, but no evidence has been found for a +7 state. The following potential scheme has been determined at pH 1:

$$At^{-} \xrightarrow{\;-0.3\;} At(0) \xrightarrow{\;-1.0\;} HOAt(?) \xrightarrow{\;-1.5\;} AtO_3^{-} \xrightarrow{\;<-1.6\;} H_5AtO_6(?).$$

It has been shown that in the absence of I_2 the predominant At(0) species are neither At_2 nor At· but may well be compounds formed between astatine and organic impurities in the solutions. Whenever possible, I_2 has been introduced to try to convert the At(0) to AtI. The photochemical oxidation of At(0) by VO_2^{+} and by Fe^{+++} has also been investigated.

Introduction

The halogen family constitutes a fertile field for the study of periodic behavior within a series of elements. To complete this series it is necessary to have knowledge of the chemistry of its heaviest member, astatine. However, astatine is an unstable synthetic element which can be worked with only at very low concentrations—concentrations much less than the impurity levels commonly present in an experimental system. Hence the desired knowledge is not easily obtained.

The oxidation potential scheme given for astatine by Latimer[3] is derived from the exploratory work of Johnson, *et al.*[4] In their work the potentials of the systems studied were not usually controlled by the presence of both halves of a reversible redox couple, and equilibria were not approached from both sides. In the present investigation we have attempted to correct these faults.

A more subtle obstacle to the interpretation of the results of Johnson, *et al.*,[4] is the uncertain nature of the "zero" oxidation state of astatine. This state is generally identified either with molecular astatine, At_2, or with the free radical At·. However, the latter seems unlikely in aqueous solution, and the expected reactivity of the former makes it probable that at least some of the "zero" state species commonly encountered are actually compounds of astatine with the various organic impurities unavoidably present in aqueous solutions. The erratic solvent extraction behavior displayed by At(0) lends support to this notion.[4] Elemental astatine should react rapidly and quantitatively with iodine to form the interhalogen AtI, and we have therefore attempted to fix the identity of At(0) by keeping aqueous solutions about 10^{-4} M in I_2 whenever possible.

Experimental

Preparation of Astatine.—The isotope At^{211}, which has a 7.2 hr. half-life, was prepared by bombardment of bismuth with alpha particles of energy less than 29 Mev. in the University of California's 60″ cyclotron. The astatine was distilled from the bismuth in air at about 750° and was collected on a water-cooled platinum plate.[5] The plate was then heated to 500° in an all-glass high-vacuum system, and the astatine was distilled into a u-tube cooled to Dry Ice temperature. The only lubricant used on joints in the path of the astatine was a completely fluorinated fluorocarbon fraction—Hooker Chemical Co.'s Fluorolube HG 1200. The astatine was washed from the u-tube with an appropriate aqueous solution, giving one ml. of concentrated stock solution about 10^{-8} M in astatine.

Analysis for Astatine.—Astatine analyses were made by counting in a scintillation counter the X-rays accompanying the electron-capture decay of the At^{211}.[6] Aliquots of solutions were counted directly, using a thallium-activated sodium iodide crystal with a built-in well, made by the Harshaw Chemical Co. Precipitates were counted as slurries in propanol. The counter was set to respond only to radiation of energy in the vicinity of the *ca.* 90 kev. k-X-ray peak, thus reducing the high background normally associated with scintillation counters.

Decay corrections were made on the basis of a carefully determined At^{211} half-life. Related assays were counted at so nearly the same time that these corrections never exceeded about 20%.

The long-lived, electron-capture isotope Bi^{207} grows into an At^{211} sample,[6] the residual bismuth X-ray activity being

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Abstracted from the Ph.D. thesis of the author, University of California (Berkeley), June 1960 (UCRL-9025). Author's present address: Argonne National Laboratory, Argonne, Illinois.

(3) Wendell M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, New York, N. Y., 1952.

(4) G. Johnson, R. Leininger and E. Segré, *J. Chem. Phys.*, 17, 1 (1949).

(5) G. Barton, A. Ghiorso and I. Perlman, *Phys. Rev.*, 82, 13 (1951).

(6) D. Strominger, J. Hollander and G. Seaborg, *Revs. Modern Phys.*, 30, 585 (1958).