The Action of Liquid Ammonia Solutions of Sodium, Potassium, and Potassium Amide upon Bismuth Oxyiodide[1]

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The successful removal of halogen from organic combination and the reduction of inorganic halides by the action of the alkali and alkaline earth metals in liquid ammonia solution[3] suggests the possibility of obtaining sub-oxides of certain metals by the reduction of oxyhalides such as bismuth oxyiodide, BiOI. The experiments described below, however, show that the compound is reduced completely in that both iodine and

instance a small and variable amount of a water-insoluble gas (hydrogen) was formed during the reaction.

Upon completion of the reaction, the insoluble reaction product was washed with liquid ammonia until colorless washings were obtained, or until the intensity of the color of the washings showed no visible decrease upon repeated washing. The solvent was then allowed to evaporate and the tube was opened for analysis.

Data relevant to these reactions are presented in Table I. The values representing analyses are the average of two or more determinations.

TABLE I

Expt.	Alkali metal	Alkali metal used, g.	Sample, g.	Bi	Alkali metal	N	%I[a] recovered from washings
			Analysis of insol. reaction product — Found, %				
			Three equivalents alkali metal				
2	K	0.333	0.5888	82.7	12.2	0.6	97.4[b]
3	K	.333	.6834	84.8	8.6	.5	97.7[b]
1	Na	.196	.5912	73.7	18.4	...	...
4	Na	.196	.3840	73.1	18.6	.5	100
			Six equivalents alkali metal				
5	K	0.666	0.7270	68.1	26.6	.3	99.2
8	K	.666	.6640	63.4	28.9	Trace	99.2
6	Na	.392	.6512	63.3	29.3	Trace	99.5
9	Na	.392	.9136	62.5	30.2	0.6	99.4

[a] Based on iodine used as BiOI. [b] Some iodine inadvertently lost prior to analysis.

oxygen are removed by the alkali metal. It might be expected that the amide ion, NH_2^-, would be more selective, since it has been shown to be a mild reducing agent.[4] However, KNH_2 undergoes simple metathesis to form $BiONH_2$.
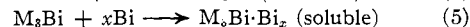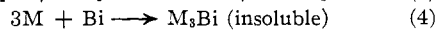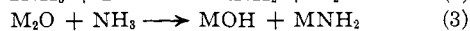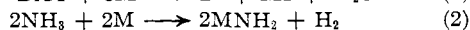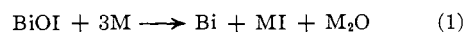
Experimental

The Action of Sodium and Potassium in Liquid Ammonia on Bismuth Oxyiodide

When 0.500 g. of bismuth oxyiodide (Merck c. p.) was treated with a solution of sodium or potassium (0–25°) in liquid ammonia,[5] the light red color of the oxyhalide was discharged immediately, the solid phase changed to a grayish-black color, and a small amount of a somewhat flocculent white precipitate appeared. A blue color, indicative of an excess of alkali metal, persisted for a short time when it was replaced either by a pale yellow color (3 equivalents of potassium) or by violet colors (all other cases). In every

Discussion

The data of Table I indicate that the following reactions are involved

$$BiOI + 3M \longrightarrow Bi + MI + M_2O \qquad (1)$$
$$2NH_3 + 2M \longrightarrow 2MNH_2 + H_2 \qquad (2)$$
$$M_2O + NH_3 \longrightarrow MOH + MNH_2 \qquad (3)$$
$$3M + Bi \longrightarrow M_3Bi \text{ (insoluble)} \qquad (4)$$
$$M_3Bi + xBi \longrightarrow M_xBi \cdot Bi_x \text{ (soluble)} \qquad (5)$$

The analyses of the washings for iodide ion show clearly that ammonia solutions of sodium and potassium quantitatively remove the iodine from bismuth oxyiodide (reaction 1). The evolution of hydrogen accompanying the reduction is due to the reaction between the metal and solvent, probably catalyzed by the liberated bismuth metal (reaction 2). The occurrence of reactions 2 and 3 accounts for the appearance of nitrogen (as MNH_2) in the washings.

Alkali monoxides (indicated in reaction 1) are not stable in liquid ammonia but are ammonolyzed to hydroxides (reaction 3),[6] thereby ex-

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(3) For primary references see: W. C. Fernelius and G. W. Watt, Chem. Rev., 20, 211–213, 226–232 (1937).

(4) F. W. Bergstrom and W. C. Fernelius, ibid., 12, 77 (1933).

(5) For technique see E. C. Franklin, "The Nitrogen System of Compounds," A. C. S. Monograph, 1935, pp. 317–330; W. C. Johnson and W. C. Fernelius, J. Chem. Ed., 6, 447–450 (1929).

(6) C. A. Kraus and E. F. Whyte, THIS JOURNAL, 48, 1781 (1926). For similar reactions of Rb_2O and Cs_2O see: E. Rengade, Compt. rend., 140, 1536 (1905); Bull. soc. chim., [3] 35, 775 (1906); Ann. chim. phys., [8] 11, 348 (1907).

plaining the white precipitate observed. Further, the analysis of the insoluble products indicates the presence of alkali hydroxide.

The composition of the insoluble products depends upon the nature of the alkali metal and the number of equivalents used. The pale yellow color (KNH_2) of the ammonia solution at the end of the reaction with three equivalents of potassium as well as the analytical data indicate that no insoluble bismuthide was formed. If the potassium in the insoluble product is assumed to be in the form of potassium hydroxide (in expt. 2, 12.2% potassium corresponds to 17.5% potassium hydroxide, the total analysis (100.8%) accounts for all of the sample.

When three equivalents of sodium are used, the color of the washings indicates the presence of bismuthides (reactions 4 and 5) which are sufficiently soluble to impart intense colors to the liquid ammonia.[7] The presence of an insoluble bismuthide is indicated by the following considerations. If all of the sodium in the insoluble products is assumed to be in the form of sodium hydroxide, the total of the analysis is several per cent. above 100 (expt. 4, 18.6% Na is equivalent to 32.3% sodium hydroxide and the total then equals 105.9%).[8]

When six equivalents of sodium or potassium are used, the solutions above the solids are strongly colored (violet for potassium and blue-violet for sodium). These colors grow less intense but persist throughout the washing process. The amount of bismuth present in the washings and the amount of alkali metal in the insoluble products are greater for the experiments involving six equivalents of alkali metal. A simple calculation shows that all of the alkali metal cannot be present as hydroxide (in expt. 6, 29.3% sodium is equivalent to 50.9% sodium hydroxide, and the total of the analysis would be 114.2%; in expt. 5, 26.6% potassium is equivalent to 38.2% potassium hydroxide, and the total of the analysis would be 106.6%). These data show that with excess alkali metal, bismuthides are formed and that the tendency to form bismuthides is greater for sodium than for potassium.

(7) E. Zintl, J. Goubeau and W. Dullenkopf. Z. physik. Chem., A154, 1–46 (1931), give the following data: Na3Bi, insoluble black solid; Na3Bi3, deep violet solution in liquid ammonia; Na3Bi5, brown solution.

(8) While it might be argued that the use of *exactly* three equivalents of sodium would lead to the production of metallic bismuth only, such a situation would be difficult to realize experimentally because in each reaction there is a variable quantity of alkali metal converted to amide by reaction with the solvent.

Experimental

The Action of Potassium Amide in Liquid Ammonia on Bismuth Oxyiodide

Preliminary experiments showed that bismuth oxyiodide reacts with a molar equivalent of potassium amide in liquid ammonia at or near room temperature to form a very dark red solid which decomposes slowly in the presence of liquid ammonia with liberation of elementary bismuth and which explodes violently when exposed to the air. When an excess of potassium amide is used, an identical product is obtained.

One-half gram of bismuth oxyiodide was brought into reaction with the potassium amide from 0.32 g. (large excess) of potassium. After standing for one hour, during which there was no further change, the ammonia solution was decanted and the solid (dark red with traces of black) was washed free of ammonia-soluble impurities. The ammonia was allowed to escape, the tube sealed off, evacuated, and the insoluble reaction product hydrolyzed *in vacuo* by the vapors from dilute hydrochloric acid. A clear solution and a small amount of a black insoluble solid (Bi) resulted.

Anal. Found (independent experiments), N, 5.7, 5.8. Calcd. for $BiONH_2$: N, 5.80; for BiN, N, 6.28. Analysis of the washings for iodine gave values of 99.8 and 99.7% (based on the weight of iodine in the BiOI used), thus showing conclusively that the oxyiodide was quantitatively dehalogenated.

Discussion

In view of the similarity of the properties of the product described above with those of bismuth nitride, BiN,[9] one might suspect that the following reaction had occurred

$$BiOI + KNH_2 \longrightarrow BiN + KI + H_2O$$

Water thus formed, however, would lead to the production of white ammonia-insoluble potassium hydroxide by interaction with the excess potassium amide

$$KNH_2 + H_2O \longrightarrow KOH + NH_3$$
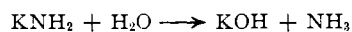
There was no evidence whatever of the appearance of potassium hydroxide among the products of the reactions under consideration. Furthermore, the analyses for nitrogen show that the product must be bismuth oxyamide rather than bismuth nitride. Accordingly, the reaction must be one of simple metathesis

$$BiOI + KNH_2 \longrightarrow BiONH_2 + KI$$
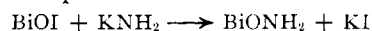
Summary

1. Bismuth oxyiodide is reduced by liquid ammonia solutions of sodium and potassium at room temperature in accordance with the equation $BiOI + 3M + NH_3 \longrightarrow Bi + MI + MOH + MNH_2$.

2. With excess alkali metal, bismuthides are formed.

3. The reaction between potassium amide

(9) E. C. Franklin, THIS JOURNAL, 27, 847 (1905).

and bismuth oxyiodide in liquid ammonia at room temperature may be represented by the
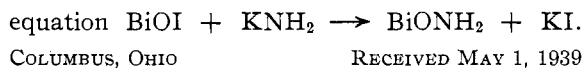
equation $BiOI + KNH_2 \rightarrow BiONH_2 + KI$.

The Ternary System: Ethyl Alcohol, Toluene and Water at 25°

By E. Roger Washburn, Albert E. Beguin and Orville C. Beckord

In order to have solubility and distribution data for this system at 25° to compare with the systems already studied[1] and others which are soon to be described, it has been found necessary to carry out this investigation. Ormandy and Craven[2] and Tarasenkov and Poloznintzeva[3] have
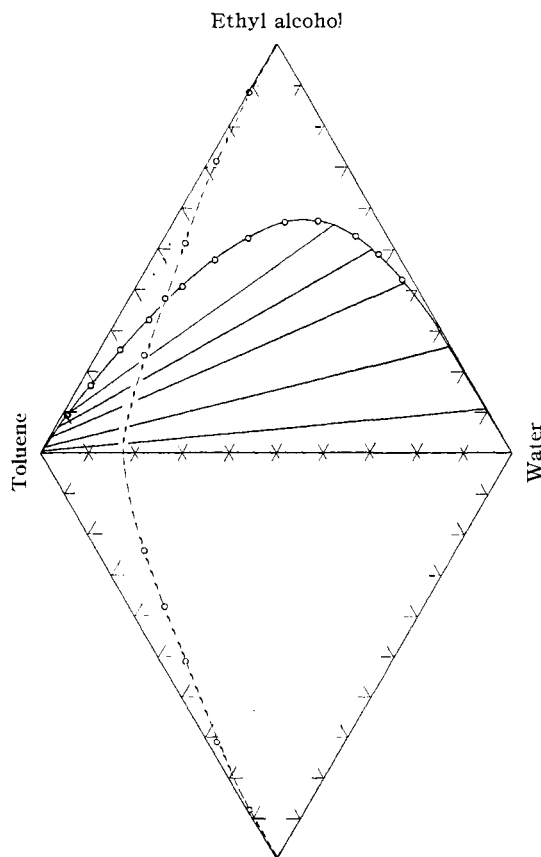
Ethyl alcohol

Fig. 1.—Solubility and conjugation curves at 25.0°.

studied this system but their studies did not include determinations of the distribution of alcohol between the toluene-rich and water-rich layers or refractive indices of the saturated solutions, and

the temperatures at which they worked were not those at which our earlier studies have been made.

Materials.—Carefully purified water was used. It was distilled from alkaline permanganate and collected while hot. A commercial grade of absolute ethyl alcohol was refluxed over lime for many hours and carefully fractionated. Its specific gravity d^{25}_4 was 0.7851 ± 0.0001, while its refractive index $n^{25}D$ was 1.35940 ± 0.00001.

Toluene of "analytical reagent grade" was dried over sodium and fractionated. This material had a specific gravity d^{25}_4 of 0.8608 ± 0.0002 and an index of refraction

TABLE I

SOLUBILITIES AND REFRACTIVE INDICES AT 25.0°

Wt. % toluene	Wt. % alcohol	Wt. % water	Refractive index
*89.84	9.36	0.81	1.4779
85.54	13.04	1.42	1.4719
*81.13	16.74	2.13	1.4660
76.33	20.66	3.01	1.4595
*70.46	25.29	4.25	1.4520
*60.61	32.66	6.73	1.4381
*49.26	40.83	9.91	1.4233
*39.40	47.37	13.23	1.4108
*29.52	52.89	17.59	1.3980
24.67	54.96	20.37	1.3920
*19.96	56.42	23.62	1.3860
17.66	56.76	25.58	1.3830
*12.94	56.66	30.39	1.3770
9.41	55.46	35.12	1.3720
* 6.37	53.04	40.59	1.3679
5.33	51.78	42.89	1.3660
* 3.72	48.89	47.39	1.3630
* 1.75	42.48	55.76	1.3585
Toluene saturated with water			1.4923
Water saturated with toluene			1.3320

TABLE II

REFRACTIVE INDICES AND CONCENTRATIONS OF ALCOHOL IN CONJUGATE SOLUTIONS AT 25.0°

Water-rich layer Refractive index	Wt. % alcohol	Toluene-rich layer Refractive index	Wt. % alcohol	Distribution ratio
*1.3389	11.0	1.4920	0.2	0.02
1.3440	19.2	1.4912	.7	.04
*1.3480	25.7	1.4903	1.3	.05
1.3540	35.2	1.4882	2.7	.08
*1.3581	41.7	1.4850	4.7	.11
1.3616	46.9	1.4841	5.3	.11
*1.3641	50.0	1.4822	6.5	.13
1.3683	53.3	1.4796	8.2	.15
*1.3724	55.6	1.4778	9.4	.17

(1) E. R. Washburn and others, This Journal, **53**, 3237 (1931); **54**, 4217 (1932); **56**, 361 (1934); **57**, 303 (1935); **59**, 2076 (1937).
(2) Ormandy and Craven, J. Inst. Petroleum Tech., **7**, 325 (1921).
(3) Tarasenkov and Poloznintzeva, J. Gen. Chem. (U. S. S. R.), **2**, 84 (1932).