From 10 g of $Ba^{13}CO_3$ and methylmagnesium iodide, acetic acid-^{13}C was prepared by the ordinary technique for the synthesis of ^{14}C-labeled carboxylic acids.[10] An aqueous solution of the acid was carefully neutralized by lithium hydroxide. After concentrating and thoroughly drying *in vacuo*, lithium acetate-^{13}C was reduced by lithium aluminum hydride (3.8 g) in dry diethylene glycol diethyl ether (150 ml) for 10 hr at 60°. The reaction mixture was treated with diethylene glycol monobutyl ether, and ethanol-1-^{13}C was distilled into a flask chilled with liquid nitrogen, under high vacuum at room temperature. It was converted into ethylene-1^{13}C by passing through a heated column of activated alumina at 400°,[11] with the aid of a nitrogen stream. The resulting gas mixture was introduced into a small excess of bromine chilled at −78°. After standing at room temperature for a while, ethylene-1-^{13}C bromide was purified by distillation *in vacuo*.

To an ether suspension of sodium amide (3.34 g) was added 9.68 g of aniline[12] at 0° for 20 min and ammonia was removed by a nitrogen stream. An ether solution of ethylene-1-^{13}C bromide was dropped into the sodium anilide solution prepared as described above, while stirring. Stirring was continued for an additional 2 hr. Acetylene-1-^{13}C was liberated from this mixture by adding 30 ml of water and then 30 ml of 2 *N* sulfuric acid, carried out with the aid of a helium stream, collected in a cold trap at −195°, and purified by repeated sublimation and degassing.

Acknowledgment.—The authors acknowledge helpful discussions with Professor M. Tsuboi, Dr. I. Kumashiro, and Dr. H. Wakamatsu. Also the authors thank Mr. M. Kainosho for his measurement of the nmr spectra and Mr. Y. Ozawa for his help in the preparation of acetylene-^{13}C.

---

[10] The procedure has been described elsewhere; for example: B. M. Tolbert, *J. Biol. Chem.*, **173**, 205 (1948).

[11] D. S. Popplewell and R. G. Wilkings, *J. Chem. Soc.*, 2521 (1955).

[12] D. Bodroux and M. Delepine, *Compt. Rend.*, **208**, 1022 (1939).

Notes

CONTRIBUTION NO. 1505 FROM THE CENTRAL
RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY,
WILMINGTON, DELAWARE 19898

The Preparation of Bronzes by an Alkali Azide–Metal Oxide Reaction

BY B. L. CHAMBERLAND

Received October 3, 1968

Metal bronzes, A_xBO_3 (where A is an alkali metal, B is W, Re, or Mo, and $0 < x < 1.0$), have been prepared in a variety of ways.[1–4] Standard methods include the reduction of alkali tungstate melts electrolytically or with H_2 or strong metallic and nonmetallic reducing agents. The most common route uses the appropriate metal. For example, tungsten bronzes may be prepared by the reaction

$$3x\mathrm{Na_2WO_4} + (6 - 4x)\mathrm{WO_3} + x\mathrm{W} \rightleftharpoons 6\mathrm{Na}_x\mathrm{WO_3}$$

The products are always nonstoichiometric ($x < 1$) and are often contaminated with tungsten metal.

In the present investigation alkali bronzes were prepared by the reaction

$$x\mathrm{AN_3} + \mathrm{MO_3} \longrightarrow \mathrm{A}_x\mathrm{MO_3} + (3x/2)\mathrm{N_2}$$

with the application of external pressure. By this technique stoichiometric compositions, AMO_3, could also be prepared.

Variations of cell edges as a function of x in the cubic K_xWO_3 solid solution are described to aid in the characterization of members of this series in future studies.

Experimental Section

Preparation of Bronzes.—The alkali azide reactions were carried out in a pressure system to minimize detonation of the azide and to prevent the volatilization of the alkali metal at high temperature. Reactions of the intimately mixed, reagent grade alkali azides and transition metal oxides were performed in open but crimped gold tubes between 100 and 3000 atm pressure in a stainless steel pressure vessel or in sealed platinum capsules at 60–65 kbars in a calibrated[2] tetrahedral anvil apparatus.[5] The temperature of operation in the low-pressure apparatus was varied between 500 and 700° and in the anvil press between 500 and 1000°. The evolution of nitrogen during the decomposition of the azides always led to the formation of microcrystalline products.

X-Ray Characterization.—X-Ray powder diffraction data were obtained with either a Debye–Scherrer or Hägg–Guinier camera using copper radiation. The patterns were read on a Mann film reader and the powder data were refined by least squares. The Nelson–Riley function was used as a parameter in the Debye–Scherrer back-reflection data. The Guinier data were obtained with monochromatic Cu $K\alpha_1$ radiation and an internal KCl standard (a = 6.2931 Å) was used.

Analyses.—Compositions of the cubic sodium tungsten bronzes were calculated from the equation relating Na content to unit cell size as derived by Brown and Banks.[6] The potassium: tungsten ratios for the K_xWO_3 products were determined by X-ray fluorescence studies. The W^{5+} content was determined by the weight gain on oxidation in an O_2–Ar atmosphere utilizing a Du Pont tga apparatus. Flame-emission studies were also made on the oxidized products and on the original bronzes dissolved in H_2O_2–NH_4OH solution.

Results

Na_xWO_3.—The Na_xWO_3 system has been extensively studied by several groups, and the cell size *vs.* composition relationship derived by Brown and Banks[6] has been most useful in determining the composition of the products directly from accurate X-ray cell dimensions. This relation, $a(\text{Å}) = 0.0819x + 3.7846$,

---

[1] L. E. Conroy and G. Podolsky, *Inorg. Chem.*, **7**, 614 (1968).

[2] T. A. Bither, J. L. Gillson, and H. S. Young, *ibid.*, **5**, 1559 (1966).

[3] A. W. Sleight and J. L. Gillson, *Solid State Commun.*, **21**, 601 (1966).

[4] T. E. Gier, D. C. Pease, A. W. Sleight, and T. A. Bither, *Inorg. Chem.*, **7**, 1646 (1968).

[5] E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **C63**, 59 (1959).

[6] B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76**, 963 (1954).

has been used in this study as a means of determining the alkali content of the products. On this basis, the compositions prepared by the sodium azide–tungsten trioxide reaction were found to fall in the range $0.70 \leq x \leq 1.01$. In all cases, the final sodium concentration was less than that of the reactants, indicating side reactions, volatilization of the alkali metal, or incomplete decomposition under the conditions utilized. The highest reactant ratios (sodium azide to oxide) and the highest pressures yielded stoichiometric $NaWO_3$. A cell edge of 3.8668 ± 0.0001 Å, obtained on a product formed at 65 kbars, corresponds to an x value of 1.004 ± 0.007 and represents a stoichiometric phase containing formally pentavalent tungsten. The reaction conditions and products formed are summarized in Table I.

TABLE I

CONDITIONS AND PRODUCTS OF THE NaN_3–WO_3 REACTIONS

Reactant ratio azide: oxide	Exptl conditions Temp, °C	Pressure, kbars	Time, hr	Cell edge a, Å	x in Na_xWO_3
1.25	750	65	2	3.8670 ± 0.0001(DS)[a]	1.006[b]
1.25	500	1.5	5	3.8556 ± 0.0003(DS)	0.867
1.20	800	65	2	3.8668 ± 0.0001(G)	1.004
1.15	800	65	2	3.8674 ± 0.0002(G)	1.011
1.10	700	0.1	5	3.8526 ± 0.0001(DS)	0.830
1.05	800	65	2	3.8659 ± 0.0002(G)	0.993
1.00	1000	65	2	3.8655 ± 0.0001(DS)	0.988
1.00	700	0.1	6	3.8399 ± 0.0001(DS)	0.675
0.90	500	1.5	5	3.8421 ± 0.0004(DS)	0.702
0.50	750	65	2	Tetr (a = 12.133 ± 0.001, c = 3.7664 ± 0.0005)(DS)	~0.43

[a] DS, Debye–Scherrer data; G, Guinier data; standard deviation given after lattice dimension. [b] As determined from the equation: $a(\text{Å}) = 0.0819x + 3.7846$.

An unsuccessful attempt was made to grow single crystals of the $NaWO_3$ composition by heating several powdered stoichiometric products to 1000° and 65 kbars, slowly cooling to 750°, and then quenching. The product was a highly sintered orange compact. A two-probe electrical measurement on this compact gave a resistivity of 4.4 ohm cm at room temperature, with little temperature dependence. Caution should be used, however, in interpreting powder compact resistivity obtained on a metallic system.

K_xWO_3.—The potassium azide–tungsten(VI) oxide reaction yielded similar results to those obtained for the sodium tungsten bronze system (Table II).

TABLE II

CONDITIONS AND PRODUCTS OF THE KN_3–WO_3 REACTIONS

Reactant ratio azide:oxide	Exptl conditions Temp, °C	Pressure, kbars	Time, hr	Cell edge a, Å	x in K_xWO_3
1.25	1000	65	2	3.9350 ± 0.0001 (G)[a]	0.90 ± 0.02
1.20	900	65	1	3.9303 ± 0.0001 (G)	0.88 ± 0.02
1.15	900	65	1	3.9290 ± 0.0002 (G)	0.86 ± 0.02
1.10	1000	65	0.5	3.9259 ± 0.0002 (G)	0.84 ± 0.03
1.00	1000	65	0.5	3.9247 ± 0.0001 (DS)	0.83 ± 0.02
0.80	1000	65	0.5	3.9235 ± 0.0005 (DS)	0.83 ± 0.03
1.05	900	65	1	Tetr (a = 12.336 ± 0.001, c = 3.847 ± 0.001) (G)	0.60 ± 0.02
0.75	800	65	2	Tetr (a = 12.336 ± 0.003, c = 3.848 ± 0.001) (DS)	0.60 ± 0.02
0.50	800	65	2	Tetr (a = 12.278 ± 0.002, c = 3.836 ± 0.001) (DS)	~0.48

[a] See footnote a of Table I. [b] As determined from the equation: $a(\text{Å}) = 0.1384x + 3.810$.

Chemical analyses were used to determine the relationship between alkali content and lattice dimensions for the cubic K_xWO_3 system. The cell edges for the cubic K_xWO_3 solid solution were found to be linear with x and to be represented by the equation $a = 0.138x + 3.810$ with a possible deviation of ±0.005 Å.

Other Systems.—The alkali azide–metal oxide reaction is also a convenient route to the synthesis of bronzes in the systems Na_xMoO_3, K_xMoO_3, Rb_xMoO_3, Na_xReO_3, and K_xReO_3. Reaction conditions for synthesis in these systems are similar to those described above (65 kbars), and reaction products are identical with those previously described.[2,3]

In addition, a new phase was discovered in the K_xReO_3 system. At low ratios of azide to oxide, the products included $KReO_4$, ReO_2, and a hexagonal, red phase which formed at the ends of the platinum reaction vessel. The lattice dimensions of this hexagonal phase corresponded to hexagonal rubidium bronze products that have been reported in the tungsten and molybdenum systems (Table III).

K_xUO_3.—The reaction of equimolar amounts of KN_3 and UO_3 at 800° and 65 kbars for 2 hr yielded a homogeneous black product. The powder pattern was indexed on the basis of a cubic unit cell with a dimension of 4.292 Å. Kovba, *et al.*,[7] and Rüdorff and Leutner[8] have reported a value of 4.290 ± 0.001 Å for KUO_3 having the cubic perovskite structure.

A similar reaction at 700° and 100 atm for 6 hr yielded a similar cubic product with a cell edge of a = 4.295 Å.

Discussion

The use of alkali azides as strong reducing agents has been discussed very little in the literature. They can be used more advantageously than alkali metals or alkaline oxides because they (1) can be easily and

---

(7) K. M. Kovba, E. A. Ippolitova, Y. P. Simanov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **120**, 1042 (1958).

(8) W. Rüdorff and H. Leutner, *Angew. Chem.*, **74**, 429 (1962); *Z. Anorg. Allgem. Chem.*, **292**, 193 (1957).

TABLE III

LATTICE DIMENSIONS OF HEXAGONAL BRONZE COMPOSITIONS

Compn	Lattice parameters, Å: *a*	Lattice parameters, Å: *c*	Ref
$Rb_{0.27}MoO_3$	7.321	7.683	*a*
$Rb_{0.27}WO_3$	7.38	7.36	*b*
K_xReO_3	7.318 ± 0.0001	7.485 ± 0.002	*c*

[a] See ref 2. [b] A. Magneli, *Acta Chem. Scand.*, **1**, 315 (1953). [c] This work.

conveniently handled in air without oxidation or hydration, (2) are relatively stable to grinding and heating under the proper conditions of applied external pressure to minimize the rapid evolution of nitrogen at and above their decomposition temperature, (3) are commercially available or can readily be prepared and purified, (4) are a source of alkali metals in a finely divided and highly reactive state, (5) are a convenient source of high-purity nitrogen which can be used for nitride formation or as a protective atmosphere during reaction of the alkali metal, (6) are readily soluble in water for easy removal from the reaction product, and, finally, (7) decompose quantitatively to the metal and nitrogen at relatively low temperatures.

High pressures were used to prepare $NaWO_3$ and molybdenum, rhenium, and cubic K_xWO_3 bronze derivatives. These products are not necessarily high-pressure phases, for molybdenum bronzes with low alkali content and monoclinic structures have been prepared[9] at atmospheric pressure.

The preparation of cubic tungsten bronzes (Na_xWO_3 and K_xWO_3), where $x = 0.90$–1.00, was achieved at the highest reactant ratios of alkali azide to tungsten(VI) oxide and at the highest pressures. As the reactant ratio decreased and the pressure and temperature remained constant, the cubic cell edge decreased until the tetragonal bronze appeared as the primary product. Variations in the temperature or pressure for a given azide to metal oxide ratio also yielded different phases. The three parameters—reactant ratio, temperature, and pressure—therefore can be varied in the preparation of different bronze products.

The isolation of bronzes with high alkali content has been greatly facilitated by the use of these high-pressure techniques. Cubic K_xWO_3, as well as cubic or tetragonal rhenium and molybdenum bronzes, has not yet been prepared at atmospheric pressure.

Several cubic sodium tungsten bronzes were isolated that appeared on the basis of a cell edge *vs.* composition plot to have an x value slightly greater than the theoretical limit of 1.00. These values, however, all fall within the standard deviation (±0.007 Å) given by Brown and Banks[6] for the composition–unit cell equation. Support of this equation was recently presented by Wechter, Shanks, and Voigt[10] from thermal neutron activation analyses on the cubic Na_xWO_3 derivatives.

---

(9) A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.*, **3**, 545 (1964).

(10) M. A. Wechter, H. R. Shanks, and A. F. Voigt, *ibid.*, **7**, 845 (1968).

Acknowledgments.—The author wishes to thank Drs. T. A. Bither and A. W. Sleight for many helpful discussions, Messrs. C. L. Hoover and H. E. Cupery for supervising the high-pressure experiments, and Miss M. S. Licis for obtaining the X-ray data.

CONTRIBUTION FROM THE BIOPHYSICS RESEARCH LABORATORY,
DEPARTMENT OF BIOLOGICAL CHEMISTRY,
HARVARD MEDICAL SCHOOL, BOSTON, MASSACHUSETTS 02115

A 3:1 8-Hydroxyquinoline-5-sulfonic Acid–Zinc Ion Complex[1a]

BY ROBERT T. SIMPSON[1b] AND BERT L. VALLEE

Received September 3, 1968

The bidentate ligand 8-hydroxyquinoline-5-sulfonic acid (L) has been reported to form 1:1 and 2:1 complexes with zinc ions.[2–5] At temperatures of 20–25° and ionic strengths of 0–0.1, the stabilities obtained were $\log K_1 = 7.54$–8.70, and $\log K_2 = 6.7$–7.5. In the course of a recent investigation of the removal of zinc by L from the bacterial enzyme alkaline phosphatase the existence of a 3:1 complex of L with ionic zinc seemed indicated, leading to a reexamination of this system. The present data demonstrate the occurrence of a 3:1 complex, similar to those previously observed for both cobalt(II) and iron(II).[5–7]

Zinc was obtained as the "SpecPure" sulfate salt from the Johnson Matthey Co., and L was obtained from the Eastman Chemical Co. All other chemicals were reagent grade and were further purified by dithizone extraction to remove trace metal contaminants.[8] Absorption spectra were obtained with a Cary Model 15 recording spectrophotometer. Potentiometric titrations were carried out using a Radiometer pH meter and titration cell assembly, under a nitrogen atmosphere at 20.0°. The titrant was added with a micrometer buret of the syringe type. All experiments were performed at an ionic strength of 0.5 *M* (NaCl). In those experiments where buffering was necessary, 0.01 *M* N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid (HEPES), pH 7.0, was utilized.

Addition of zinc to L at pH 7.0 generates a new absorption spectrum with a maximum at 370 mμ. When a constant amount of ligand is titrated with increasing

---

(1) (a) This work was supported by Grant-in-Aid HE-07297 from the National Institutes of Health of the Department of Health, Education, and Welfare. (b) Postdoctoral Fellow of the National Institute of General Medical Sciences, National Institutes of Health, 1964–1967.

(2) (a) A. Albert, *Biochem. J.*, **54**, 646 (1953); (b) L. E. Maley and D. P. Mellor, *Australian J. Sci. Res.*, *A*, 579 (1949).

(3) R. Nasanen and E. Uisitalo, *Acta Chem. Scand.*, **8**, 112 (1954).

(4) R. Nasanen and E. Uisitalo, *ibid.*, **8**, 835 (1954).

(5) C. F. Richard, R. I. Gustafson, and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 1033 (1959).

(6) J. C. Tompkinson and R. J. P. Williams, *J. Chem. Soc.*, 1153 (1958).

(7) J. C. Tompkinson and R. J. P. Williams, *ibid.*, 2010 (1958).

(8) R. E. Thiers in "Methods of Biochemical Analysis," Vol. 5, D. Glick, Ed., Interscience Publishers, New York, N. Y., 1957, p 273.