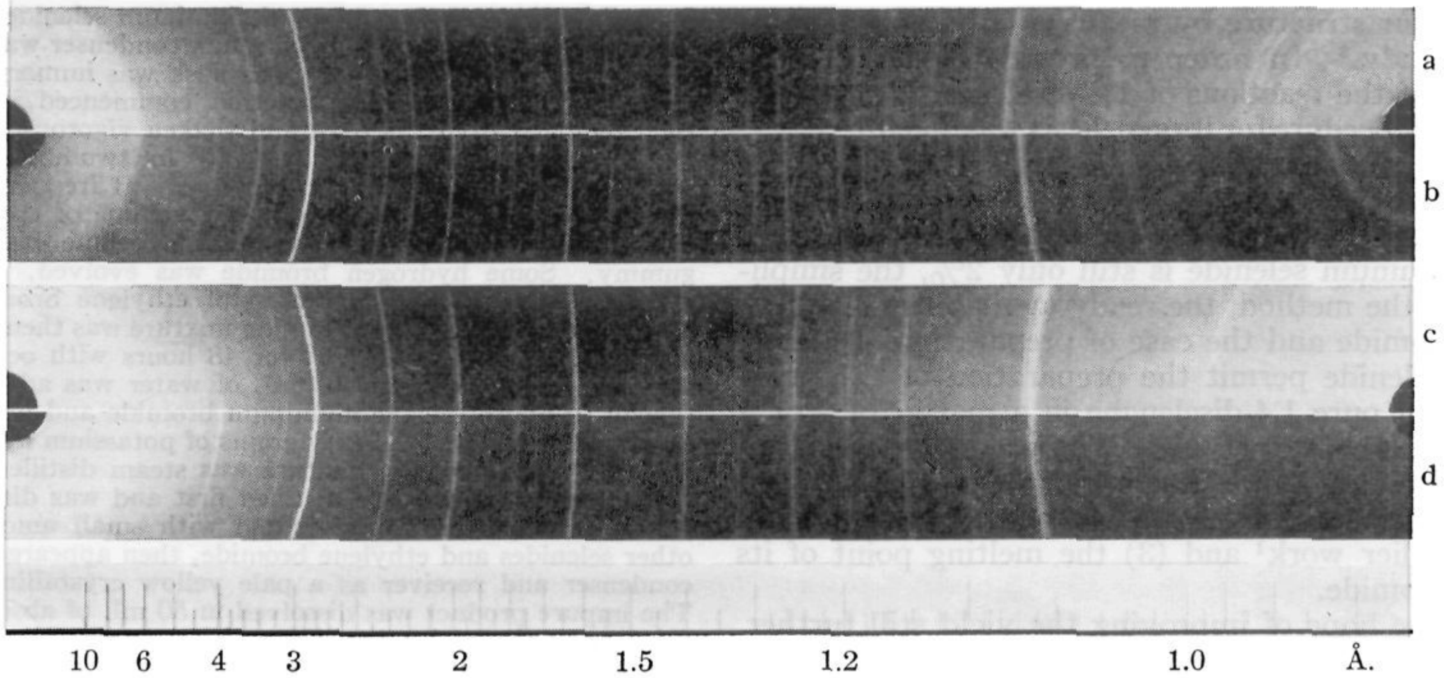

Fig. 1.—Comparison of X-ray diffraction patterns of Ba–Fe–oxide and $BaTiO_3$ polymorphs; camera radius 57.3 mm., filtered Fe radiation: a, $BaTiO_3$, hex.; b, Ba–Fe–oxide, hex.; c, $BaTiO_3$, tetr.; d, Ba–Fe–oxide, tetr.

the $BaCO_3$–Fe_2O_3 system by Erchak, Fankuchen and Ward.[1] The X-ray diffraction pattern of their product, and the approximately ABO_3 composition, suggested to those authors a perovskite-type structure. The presence of certain extra lines in the pattern, however, led them to adopt instead a larger cubic cell composed of eight perovskite basic units. This larger face-centered cell (a_0 = 8.05 Å.) was interpreted as due to an ordered distribution of oxygen vacancies corresponding to the chemically-indicated composition $Ba_8Fe_8O_{21}$. The diffraction pattern of the reaction product recently obtained by us was found to be essentially the same as that reported by the authors mentioned above. Studied in the light of information now available concerning the polymorphic structures exhibited by $BaTiO_3$, however, the pattern of this product can be indexed in the hexagonal system, and in fact, it matches very well the pattern of the hexagonal polymorph of $BaTiO_3$ (Fig. 1).

Encouraged by these results, we investigated the possibility of the occurrence of the other analogous polymorphs with cubic or pseudo-cubic structures. Firing the hexagonal barium iron oxide at 1275° in oxygen and slow-cooling resulted in the tetragonal polymorph. Here also, a comparison with the corresponding X-ray diffraction pattern of tetragonal $BaTiO_3$ showed good agreement. A few weak extra lines, however, indicate the presence of some hexagonal phase material, probably due to the slow-cooling. The evaluation of the hexagonal and tetragonal forms of the barium iron oxide and the comparison with $BaTiO_3$ are shown in Table I. The unit cell dimensions determined show that in both cases the barium iron oxide analogs are slightly smaller than those of $BaTiO_3$. This indicates that the iron ion is slightly smaller than the corresponding titanium ion.

TABLE I

Unit cell	Barium iron oxide	$BaTiO_3$	Structure
a_0, Å.	5.68	5.74	
c_0	13.86	14.05	Hexagonal
c_0/a_0	2.44	2.45	
a_0, Å.	3.98	3.99	
c_0	4.01	4.03	Tetragonal
c_0/a_0	1.01	1.01	

The ideal chemical formula $BaFeO_3$, barium metaferrate(IV), implies an iron oxidation state of four, which is rare. The more common iron valence, three, would lead to compositions lying in the range between $BaFeO_{2.5}$ and $Ba_{1.2}Fe_{1.2}O_3$, but neither a 16% deficiency of oxygen, nor a 20% surplus of barium is likely in a stable perovskite structure. A more plausible alternative is the co-presence of Fe(III) and Fe(IV) in the same structure with a corresponding increase in the number of oxygens per molecule toward three. This alternative is favored by the results of preliminary measurements of electrical conductivity on pellets of the reaction product. It is worthwhile to note that of the two polymorphic modifications of barium iron oxide, the hexagonal form seems to be more stable at low temperatures, the tetragonal at higher, which is just the reverse of the situation in the $BaTiO_3$. In a future paper the stability, formation conditions and electrical and magnetic properties of these barium iron oxide polymorphs will be described in greater detail.

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[1] M. Erchak, Jr., I. Fankuchen and R. Ward, THIS JOURNAL, **68**, 2085 (1946).

A New Synthesis of 1,4-Diselenane. The 1,1,4,4-Diselenane Tetrahalides

BY J. D. MCCULLOUGH AND N. W. TIDESWELL

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The cyclic selenide 1,4-diselenane was first prepared by the reaction of lithium selenide on β,β'-dichlorodiethyl selenide in anhydrous acetone.[1] Although the yield was only 0.3%, the substance was unambiguously identified through selenium analysis and a complete determination of its crystal and

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[1] E. S. Gould and J. D. McCullough, THIS JOURNAL, **73**, 1105 (1951).

molecular structure by means of an X-ray diffraction study.[2] In order to provide material for a study of the reactions of 1,4-diselenane, a more efficient procedure for its synthesis was sought.

The most promising of several trial procedures involved the direct reaction of aluminum selenide with ethylene bromide. Although the yield based on aluminum selenide is still only 2%, the simplicity of the method, the ready availability of ethylene bromide and the ease of preparation of aluminum selenide permit the preparation of two-gram yields of pure 1,4-diselenane in a matter of 2 or 3 days of laboratory time. The product was identified through: (1) its melting point, (2) a mixed melting point with a portion of the product from the earlier work[1] and (3) the melting point of its tetrabromide.

In the hope of improving the yield still further, magnesium selenide and ferrous selenide were also tried, but in both cases the yield of the desired product was negligible. Also, in order to test the versatility of the reaction, propylene bromide and a mixture of *cis-* and *trans*-2-butene dibromides reacted with aluminum selenide. In both cases the reaction was vigorous and went out of control. Due to this fact and the complexity of the anticipated products, these reactions were not investigated further at this time but were set aside for future study.

It appears that the low yield of the reaction between aluminum selenide and ethylene bromide is due to the formation of an adhering coating of aluminum bromide on the aluminum selenide. It is possible that the yield of 1,4-diselenane could be further improved by avoiding this coating since neither starting material is completely consumed when the reaction stops. Further work in this direction is planned.

Halogens react with 1,4-diselenane to form solids which presumably are 1,1,4,4-diselenane tetrahalides. These latter substances are insoluble in the common organic solvents and are accordingly precipitated quantitatively when solutions of the components are mixed. The extreme insolubility of these halides in carbon disulfide and carbon tetrachloride (in which most dialkyl and diaryl selenium dihalides are quite soluble) makes the determination of their equivalent weights by the method of McCullough, Campbell and Krilanovich[3] practically impossible. The composition of each of these compounds was accordingly determined by weighing the tetrahalide formed when a 5% excess of the halogen was added to a weighed sample of 1,4-diselenane dissolved in carbon tetrachloride. An X-ray diffraction study of the tetrahalides is planned.

Experimental

Aluminum Selenide.—One hundred grams of powdered selenium and forty grams of powdered aluminum were thoroughly mixed and ignited in 20-g. portions in a porcelain crucible. Excess aluminum rose to the surface of the fused mixture and was removed after cooling. The product was ground to a powder and stored in a tightly stoppered bottle.

Ethylene Bromide.—Eastman Kodak Co. white label ethylene bromide was used without further purification.

1,4-Diselenane.—To 100 g. of aluminum selenide in a 1-liter erlenmeyer flask fitted to a reflux condenser was added 200 g. of ethylene bromide. The flask was immersed in a steam-bath until vigorous reaction commenced. It was then removed from the bath and shaken vigorously. The temperature was maintained at 70–80° for two hours during which the sample was shaken vigorously at frequent intervals. A considerable increase in the volume of the aluminum selenide occurred and the solid became black and gummy. Some hydrogen bromide was evolved, presumably due to dehydrobromination of ethylene bromide by aluminum bromide. The reaction mixture was then kept in a bath at approximately 75° for 48 hours with occasional shaking. After cooling, 400 ml. of water was added cautiously to hydrolyze the aluminum bromide and unreacted aluminum selenide. Twenty grams of potassium hydroxide was then added and the mixture was steam distilled. Unreacted ethylene bromide distilled first and was discarded. The 1,4-diselenane, contaminated with small amounts of other selenides and ethylene bromide, then appeared in the condenser and receiver as a pale yellow crystalline solid. The impure product was dissolved in 50 ml. of absolute alcohol and refluxed for 5 minutes with 1 g. of potassium hydroxide to hydrolyze any ethylene bromide or halogenated selenides present. Seventy-five ml. of water was then added and the mixture allowed to stand for one hour. The 1,4-diselenane was filtered out, refluxed with alcoholic KOH, and again precipitated by addition of water. The product was twice recrystallized from ethanol and dried over calcium chloride. The yield was 2 g.

Melting points: product from new synthesis, 112.5–113.5°; product from previous work,[1] 113.0–113.5°; mixture (1:1) of products from the two methods, 113.0–113.5.

1,4-Diselenane Tetrachloride.—To 0.5289 g. of 1,4-diselenane in 30 ml. of carbon tetrachloride was added 8.1 ml. of a 0.64 *M* solution of chlorine in that solvent. The precipitate was collected in a sintered glass crucible, washed with 20 ml. of carbon tetrachloride to which 0.5 ml. of the chlorine solution had been added, then air-dried to constant weight; yield of 1,4-diselenane tetrachloride, 0.884 g.; theoretical yield, 0.8794 g.; calculated ratio of moles of chlorine per mole of 1,4-diselenane, 2.02. The white solid melted at 178–181° dec.

1,4-Diselenane Tetrabromide.—The above procedure was used, starting with 0.6595 g. of 1,4-diselenane and 10.5 ml. of 0.62 *M* bromine solution. The yield of tetrabromide was 1.610 g. compared to a theoretical yield of 1.645 g. The calculated ratio of moles of bromine per mole of 1,4-diselenane is 1.93. The pale yellow solid melted at 148–151° dec.

1,4-Diselenane Tetraiodide.—The same procedure was again used, starting with 0.3765 g. of 1,4-diselenane and 32.5 ml. of 0.114 *M* iodine solution. The yield of tetraiodide was 1.264 g., compared to a theoretical yield of 1.270 g. The calculated ratio of moles of iodine per mole of 1,4-diselenane is 1.99. The brick-red solid melted at 150–151° dec.

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[2] R. E. Marsh and J. D. McCullough, THIS JOURNAL, **73**, 1106 (1951).

[3] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

Effect of Temperature on the Absorption Spectrum of Iodine in the Alkyl Iodides[1]

BY DONALD E. SCHULER AND ROBERT H. SCHULER

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There has been in recent years a greatly renewed interest in the general problem of the solvation of iodine, particularly in regard to the resulting effect on the absorption spectrum of iodine solutions.[2,3] Among the solvents in which solvation is pro-

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[1] From the M.S. Dissertation of D. E. Schuler, Canisius College, June, 1952.

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949); see R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952), for a comprehensive summary of electron donor-acceptor interactions.

[3] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).