[Contribution from College of St. Thomas,[a] Macalester College[b] and Economics Laboratory, Inc.[c]]

Preparation and Properties of the Sodium Hypochlorite Complex of Trisodium Orthoarsenate

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Received April 2, 1956

A sodium hypochlorite complex hydrate of trisodium orthoarsenate was prepared by reaction of sodium hydroxide, disodium monohydrogen orthoarsenate heptahydrate and sodium hypochlorite. From analytical data obtained, the theoretical formula $(Na_3AsO_4 \cdot 11H_2O)_6NaOCl \cdot NaCl$ has been assigned. Melting point, density, solubility in water and extinction coefficient have been determined. Stability as revealed by hypochlorite content was followed for a period of five weeks. X-Ray diffraction photographs of the compound are completely different from those of the unchlorinated $Na_3AsO_4 \cdot 12H_2O$, but quite similar to the apparently isomorphous chlorinated trisodium orthophosphate.

In the course of an investigation of possible inorganic sodium hypochlorite complexes of greater stability and hypochlorite content than the well known commercial chlorinated trisodium orthophosphate, the complexes with trisodium orthoarsenate were found to possess sufficient stability to warrant further study. Bell[1] has reported a number of complex hydrates of trisodium orthophosphate. He states that trisodium orthophosphate forms complexes of the general formula $(Na_3PO_4 \cdot xH_2O)_nNaY$, where n may have values from 4 to 7, x is 11 or 12, and Y is one of a limited number of monovalent anions, and suggests that the ability of the complex to retain the molecule of salt, NaY, depends on its resistance to dehydration. In view of this and the obvious similarities of orthophosphates and orthoarsenates, it was decided to attempt a preparation of trisodium orthoarsenate in the presence of NaOCl to determine whether a similar complex could be formed.

Experimental

Methods of Preparation.—For the preparation of such a compound several methods were considered. It was believed that the purest compounds might be prepared by crystallization from a dilute solution of NaOCl containing a three to one mole ratio of Na_2O to As_2O_5. However, it was found that the crystalline product contained only a few tenths of a per cent. of NaOCl; variation of the ratios of reactants over wide ranges, the NaOCl up to the maximum available, approximately a 15% solution, failed to increase the hypochlorite content retained by the crystalline product. While this method proved to be unsuccessful for the original preparation, recrystallization from hypochlorite solution does improve the physical properties of the compound made by other methods.

The "batch" method, in which theoretical amounts of NaOH, As_2O_5, NaOCl and a slight excess of water are ground together continuously during the vigorous exothermic reaction, proceeds to completion, without loss of chlorine, and yields a dry solid. However, the reaction is so rapid that thorough mixing is probably not achieved, and consequently the product lacks uniformity required for obtaining satisfactory physical and analytical data.

The "melt" method was the method used for the preparation of the compound reported. The calculated amount of $Na_2HAsO_4 \cdot 7H_2O$, Reagent Grade, 67.60 g., was weighed into a small beaker and dissolved in 75 ml. of hot water; 17.75 g. of 47.1% NaOH solution was weighed into another beaker. (This is the calculated amount, together with the NaOH in the hypochlorite solution, for the theoretical formula proposed.) The contents of these beakers were transferred to a 500-ml. casserole and rinsed with 25 ml. of hot water. This solution was then concentrated by evaporation over a steam-bath until nearly ready to solidify, when the calculated amount of sodium hypochlorite solution, 58.1 ml. of 11.8% NaOCl and 0.6% NaOH, heated to 60° was added rapidly. The solution was heated and stirred for 20 minutes to ensure complete uniformity and then poured into a large, cold evaporating dish to crystallize. Upon cooling, the long needle-like white crystals could be separated from the mother liquor, which was found to contain little excess NaOCl. A brief period of evaporation before pouring into the cold dish for crystallization will yield a crop of crystals without mother liquor, but the crystals are not as well defined as when prepared in the above manner.

Analytical Data.—(1) Average per cent. loss in weight for a number of samples was found to be 48.28%. The loss in weight represents chlorine in NaOCl and total water.

(2) Per cent. NaOCl for a number of samples was found to be approximately 3% which represents 1.43% chlorine. Subtracting this from the total loss of 48.28% yields 46.85% for per cent. water.

(3) Per cent. As_2O_5 was determined by titration of the liberated iodine in 4 N HCl solution,[2] and subtracting the calculated amount of hypochlorite (in (2) above). Average value from a number of samples was 26.16%.

(4) Total chlorine for determination of per cent. NaCl. In weakly alkaline solution the reaction is quantitative[3]

$$NaOCl + H_2O_2 \longrightarrow O_2 + H_2O + NaCl$$

A weighed sample of the product was dissolved in water and adjusted to a pH of 8 with a few drops of dilute HNO_3. Then 5 ml. of 3% H_2O_2 (free of chloride) was added and later 10 ml. of 5% HNO_3, and then an excess of $AgNO_3$ for complete precipitation. The rest of the procedure for chloride determination was that of Willard and Furman.[4] From the known NaOCl present in the sample, and the total chlorine, the average per cent. NaCl for a number of samples was found to be 2.23%.

Table I

Time–Temperature Cooling Curve Data for Three Preparations of Chlorinated Trisodium Arsenate

Time, min.	Temperature, °C. I	II	III
0.0	85.0	85.0	83.0
0.5	83.9	83.2	81.8
1.0	82.9	82.3	80.9
1.5	81.9	81.0	80.2
2.0	81.0	80.2	80.0
2.5	79.9	80.0	80.0
3.0	79.0	80.0	79.9
3.5	79.5	79.9	79.5
4.0	79.5	79.7	79.0
4.5	79.5	79.5	78.3
5.0	79.3	79.0	77.2
5.5	79.1	77.9	77.0
6.0	78.7	77.2	76.4
6.5	78.3	76.7	75.7
7.0	77.3	75.7	75.0
7.5	76.9	74.8	73.0
8.0	76.3	73.0	71.6

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(1) R. N. Bell, *Ind. Eng. Chem.*, **41**, 2901 (1949).

(2) I. M. Kolthoff, *Pharm. Weekblad*, **56**, 1322 (1919).

(3) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," 3d Ed., The Macmillan Co., New York, N. Y., 1952, p. 560.

(4) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 3d Ed., D. Van Nostrand Co., New York, N. Y., 1940, p. 320.

(5) Assignment of theoretical formula. The above analytical data, *viz.*, NaOCl, 3.00%, NaCl 2.23%, H_2O 46.85%, As_2O_5 26.16%, Na_2O 29.75% (by difference only), converted to moles, gives 1.03, 1.00, 68.20, 2.98, 9.20, respectively, whose nearest whole number ratios are 1:1: 68:3:9. The 68 for water has to be adjusted to yield the formula: $(Na_3AsO_4 \cdot 11H_2O)_6 \cdot NaOCl \cdot NaCl$.

(6) Cooling curves were determined in the usual manner, the data shown in Table I being obtained. Run III of this table shows temperatures obtained after melting, cooling and remelting the sample repeatedly. Melting points were also determined for a number of samples in conventional melting point tubes, the temperatures of melting being between 79 and 81°.

(7) The solubility of the compound in water at 30° was determined by withdrawing 5-ml. samples of the saturated solution through a cotton filter and evaporating to dryness and then igniting at the full heat of a Meeker burner as was done for determining weight loss as shown above. From the weight of this residue the calculated solubility at 30° is 44.46 g./100 ml.

(8) Density was determined with a West pycnometer using benzene, the value 1.7914 at 30°/4° being obtained.

(9) X-Ray diffraction photographs of chlorinated trisodium arsenate and chlorinated trisodium phosphate were taken and the "*d*" values determined from these photographs. These values for the strongest lines are as follows: for the chlorinated trisodium arsenate, prepared by the "melt" method described herein, 10.1, 5.98, 5.49, 4.40, 4.06, 3.71, 3.35, 3.01, 2.73, 2.48; for a sample of chlorinated trisodium phosphate obtained from the Blockson Chemical Company, Joliet, Illinois, 10.3, 5.98, 5.43, 4.38, 4.01, 3.70, 3.34, 3.01, 2.72, 2.46.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Crystal Structure of *trans*-Ethanediseleninic Anhydride

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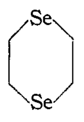
RECEIVED APRIL 30, 1956

The crystal structure of *trans*-ethanediseleninic anhydride ($C_2H_4Se_2O_3$) has been determined. This compound, the first alkaneseleninic anhydride to be described, crystallizes in the orthorhombic system, space group D^{14}_{2h}-P_{bcn}; there are four molecules in the unit cell. The molecule is a five-membered heterocyclic ring and has two types of selenium-to-oxygen bonds. The Se–O bonds within the ring (1.82 ± 0.03Å.) are considerably longer than the "exocyclic" Se–O bonds (1.61 ± 0.03 Å.). The very short intermolecular selenium-to-oxygen distances (2.70 ± 0.10 Å. and 3.11 ± 0.03 Å.) indicate strong intermolecular attraction which is, in turn, reflected in the unusually high density (2.92 g./cc.) of the crystal.

The oxidation of 1,4-diselenane (I) with 40% peroxyacetic acid yields several solid products. Among these was the expected product, the dioxide II, and there was also isolated a small quantity of a dense white solid whose composition suggested the seleninic anhydride structure III. The latter compound, presumably arising from oxidative degradation of the diselenane ring system, was of interest since it would represent the first alkaneseleninic anhydride to be reported[1] and also the first example of a five-membered ring containing two non-adjacent selenium atoms. Furthermore, it seemed surprising that an anhydride could be recovered unchanged by recrystallization from aqueous methanol. Finally, if the configuration of the three bonds about the selenium atom is pyramidal, this compound should be, to our knowledge, the first example of a monocyclic acid anhydride capable of existence in *cis*- and *trans*- forms. In view of these points, a confirmation of the assigned structure by X-ray diffraction was undertaken.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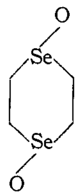
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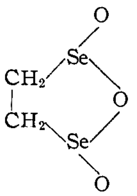
III

Experimental

Preparation of Sample.—To 1 cc. of glacial acetic acid was added 200 mg. of 1,4-diselenane.[2] The mixture was cooled to 0°, and 1.0 cc. of a solution of 40% peroxyacetic acid in glacial acetic was added dropwise. The mixture was allowed to stand 10 minutes, and 2 cc. of ice-water was added. The solution was extracted 3 times with 10-cc. portions of ether, the ether extracts being discarded. The aqueous layer was evaporated to dryness *in vacuo* at 25°. The residue was dissolved in a minimum volume of water at 45°, and the solution quickly diluted with eight times its volume of boiling methanol. Slow cooling yielded 30 mg. (14%) of the anhydride. The compound darkens at 95° to yellow and melts in the range 100–102°.

Anal. Calcd. for $C_2H_4O_3Se_2$: Se, 67.5. Found: Se, 67.5.

(In this preparation, the main product, 1,4-diselenane dioxide (II), remains in the mother liquor. If, however, ethanol be used as a crystallization solvent, the dioxide crystallizes, leaving the anhydride in the mother liquor.)

The crystals of the anhydride were prism-shaped with well developed faces of the type (110) and (011). Two determinations of density by the flotation method (using mixtures of CCl_4 and CH_2I_2) gave the values 2.96 and 2.87 g./cc. Since the anhydride decomposed slightly upon standing in warm humid air for a week, the individual crystals to be studied were enclosed in small, thin-walled glass capillary tubes. The two crystals upon which our data are based were approximately 0.2 × 0.2 × 0.25 mm. and 0.25 × 0.25 × 0.3 mm.

X-Ray Diffraction Data.—Precession photographs of the zones (*hk*0), (*h*0*l*), and (0*kl*), taken with filtered molybdenum radiation, were used to determine the structure. Two exposures (one 3 hours, one 48 hours) of each of these zones were taken. These photographs gave the orthorhombic cell dimensions (Mo Kα taken as 0.708 Å.): a = 4.64 Å., b = 9.96 Å., c = 11.22 Å. (each ±0.5%), V = 518.5 Å.[3] This volume, together with the density 2.92 g./cc., yields the figure 3.91 molecules per unit cell.

The intensities of the diffraction spots were estimated visually, using a calibrated comparison strip, and were corrected for Lorentz and polarization factors in the usual way.

The rather high value of the absorption coefficient calculated for this compound (μ_{Mo} = 151 cm.$^{-1}$) indicates that absorption effects cannot be ignored. However, the irregular shapes of our crystals prevented direct calculation of absorption corrections as such, the result being that absorption effects became incorporated in our empirical "temperature factors," obtained later in the course of the structure determination.

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[1] To our knowledge, the only seleninic anhydride described is benzeneseleninic anhydride, reported by H. W. Doughty, *Am. Chem. J.*, **41**, 336 (1909).

[2] J. D. McCullough and N. Tideswell, THIS JOURNAL, **76**, 3091 (1954).