

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Cyanates and Thiocyanates of Phosphorus, Arsenic and Antimony

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Forbes and Anderson¹ recently isolated cyanates or isocyanates, or both, of silicon, phosphorus and boron by the action of silver (iso)cyanate upon the corresponding chlorides. In the present report similar halogenoid derivatives have been prepared from POCl_3 , AsCl_3 and SbCl_3 , and some interesting transformations have been noted in the compounds thus obtained. Thiocyanates, $\text{PO}(\text{SCN})_3$ and $\text{As}(\text{SCN})_3$, have been prepared also.

Phosphoryl Isocyanate and Cyanate

Preparation.—The preparation was made in two sections, each of which gave about the same yield of product. A total of 300 g. of powdered silver (iso)cyanate and 200 g. of phosphoryl chloride in 225 ml. of pure benzene was used in a forty-four hour reflux, with occasional shaking. Filtration removed silver chloride and phosphoryl cyanate, $\text{PO}(\text{OCN})_3$, a hydrolyzable yellowish compound (from the thermal transformation of soluble liquid into insoluble solid). After removal of benzene, there remained 12.5 g. of a colorless liquid: an 11% yield of isocyanate. Formation of the insoluble cyanate was the chief reason for the low yield. Lead cyanate reacted extremely slowly with phosphoryl chloride under similar conditions. Vacuum distillation of $\text{PO}(\text{NCO})_3$ was necessary. *Analysis* of the purified material: a weighed sample was hydrolyzed in a large excess of 3 *N* sodium hydroxide, and then heated in 6 *N* nitric acid for an hour; ammonium phosphomolybdate was precipitated from a volume of 100 ml., 2 *N* in nitric acid. $\text{PO}(\text{NCO})_3$: phosphorus found 17.4, 17.7%, average 17.6%; calculated 17.90%. The molecular weights were determined by the Dumas method, with determination and subtraction of the weight of phosphorylcyanate, non-volatile, from thermal transformation of the isocyanate during the experiment. Found: 171.4, 169.9, average 170.7; calculated 173.04.

Properties.—The m. p. was $5.0 \pm 0.5^\circ$. Density measurements were obtained by the delivery from a pipet; the index of refraction was obtained at 20° using an Abbé refractometer, with thermostated prism. Boiling points at various pressures were obtained via the dynamic method in an all glass apparatus, with a calibrated thermometer. A slight uncertainty exists, because of a non-volatile form, $\text{PO}(\text{OCN})_3$, possibly having a slight solubility; this cyanate is produced very slowly by heating the isocyanate above 100° .

A summary of the data obtained: colorless compound; b. p. (760 mm.) $193.1 \pm 2^\circ$; m. p. $5.0 \pm 0.5^\circ$; vapor pressure, $\log_{10} p$ (mm.) = $9.1682 - 2931/T$; $\lambda_v = 13,410$ cal.; $\lambda_v/T = 28.8$ cal./deg.; density, 1.570 ± 0.003 g./cc.; refractive index 1.4804; vapor pressure at 25° , calculated 0.2 mm. As a lachrymator it is much weaker than phosphoryl chloride.

Non-volatile Form; Phosphoryl Cyanate.—This form was prepared from pure phosphoryl isocyanate by heating at 156° for five hours, and then removing unchanged $\text{PO}(\text{NCO})_3$ in a high vacuum. Analysis for phosphorus, 17.6%; calculated 17.90%. This cyanate was a light yellow powder without evident crystalline structure. A gas was evolved when the substance was treated with acid. About 2% of the isocyanate was converted into an insoluble form in twenty hours at 100° . This cyanate darkened when warmed in a high vacuum, and was non-volatile. It has been previously¹ shown that phosphorus triisocyanate and its insoluble product are in equilibrium; one form can be converted into another—high temperatures favor the liquid form.

Phosphoryl Thiocyanate²

Preparation.—The preparation was made with benzene as solvent, to preclude loss of any low-boiling isothiocyanate. One hundred and ten grams of powdered silver thiocyanate, 80 g. of phosphoryl chloride, and 130 ml. of pure benzene were heated forty hours on a steam-bath, with shaking. Twenty grams of product was obtained by fractional distillation at diminished pressure. The middle fraction was redistilled and the new middle fraction taken for measurements.

Analysis.—A weighed sample was hydrolyzed in 6 *N* nitric acid—since the hydrolysis in water alone would have been very slow. $\text{PO}(\text{SCN})_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 3\text{HSCN}$. Nitric acid, especially hot concentrated acid, converts thiocyanic acid into ammonium acid sulfate and hydrocyanic acid. The solution was kept at 100° for a half hour, to ensure presence of phosphorus at its highest oxidation level. Ammonium phosphomolybdate was precipitated in a volume of 100 ml., 2 *N* in nitric acid. Phosphorus found 13.9, 13.5, 14.2%, average 13.9%; calculated 14.00%. Molecular weights were obtained from the freezing point lowering of benzene; found 222, 232, average 227; calculated 221.2.

Properties.—The purest liquid when freshly prepared was colorless, although old samples tended to become orange colored. This liquid supercooled below 0° before freezing; m. p. $13.8 \pm 1.0^\circ$; boiling point $300.1 \pm 2^\circ$; slight decomposition and darkening set in during vapor pressure determinations, especially at temperatures over 250° . Vapor pressure equation: $\log_{10} P = 8.5330 - 3240/T$; $\lambda_v = 14,820$ cal.; $\lambda_v/T = 25.8$ cal./deg.; density 1.484 g./cc.; isomeric changes, none. Thiocyanate test on 0.01 ml. of pure fresh liquid, with acidified ferric nitrate was very strong. Vapor pressure at 25° : calculated 0.005 mm.; no lachrymatory properties.

Arsenic Tricyanate

Preparation.—The analog of phosphorus tricyanate¹ was prepared by reaction of 45 g. of silver (iso)cyanate and 17 g. of arsenic trichloride in 100 ml. of benzene (all operations

(1) Forbes and Anderson. *THIS JOURNAL*, **62**, 761 (1940).(2) Previously prepared in solution, only: Dixon, *J. Chem. Soc.*, **79**, 541 (1901).

were carried out under a hood, with special precautions to avoid inhalation or physical contact with poisonous arsenic compounds). The reaction was complete after thirty minutes of reflux on a steam-bath, with much shaking. Filtration yielded a very pale yellow solution; evaporation of the solution under diminished pressure resulted in a white solid of only moderate solubility in benzene at 30°. Upon warming the solid melted. Attempts to distil the liquid were made at various pressures: at 1 atmosphere, little distillation, product isomerizing from $\text{As}(\text{NCO})_3$ into non-volatile $\text{As}(\text{OCN})_3$ as shown later; at 150 mm., in an all-glass system, 10–11 g. or 60% distillation; at 73 mm. and 150.7°, about 80% distillation. Two products were obtained, volatile $\text{As}(\text{NCO})_3$, and non-volatile $\text{As}(\text{OCN})_3$; both liberated carbon dioxide with water or acid.

Analysis was accomplished by hydrolysis of weighed pellets in hydrochloric acid. $\text{As}(\text{NCO})_3 + 3\text{HCl} = \text{AsCl}_3 + 3\text{HNCO}$. Then $3\text{HNCO} + 3\text{H}_2\text{O} + 3\text{HCl} = 3\text{NH}_4\text{Cl} + 3\text{CO}_2$. The solution was made alkaline, then acid, and finally a large excess of sodium bicarbonate was added. Arsenic was determined by titration with standard iodine solution, with addition of starch indicator near the end-point. Found, arsenic 37.28, 37.20%, average 37.24; calcd. 37.28%. This end-point is quite sharp at room temperature.

Properties.—Because of the poisonous nature of the arsenic compound and because of its instability, only limited observations were made. A boiling point at 760 mm., $224.0 \pm 2^\circ$, was obtained by rapid comparison with that of naphthalene under similar conditions, and with the same thermometer; m. p. $97.1 \pm 1^\circ$. Color was pure white; crystalline form, long needles. Vapor pressure equation, from 73 and 760 mm. points: $\log_{10} P = 8.7638 - 2924/T$. At room temperature the vapor pressure of the solid is estimated at 0.05 mm. Needles were obtained by cooling a saturated benzene solution. Approximately: $\lambda_v = 14,800$ cal.; $\lambda_v/T = 26.9$ cal./deg.

Non-volatile Form; Arsenic Cyanate.—This was prepared by refluxing $\text{As}(\text{NCO})_3$ at about 230°, with fairly rapid production of the solid form; excess $\text{As}(\text{NCO})_3$ was removed in a high vacuum. Heating of the solid form, presumably $\text{As}(\text{OCN})_3$, at 0.001 mm. pressure resulted only in darkening, without volatilization.

Arsenic Thiocyanate

Miquel³ thought he had volatilized a few centigrams of this compound when he heated arsenic trichloride with lead thiocyanate. He may have obtained a mixture of arsenic trioxide with some diluent. A reaction of arsenic trichloride with silver thiocyanate, in benzene as solvent, did produce a substance containing arsenic and thiocyanate. This supposed arsenious thiocyanate was soluble in benzene, but did not crystallize from benzene. Upon heating in a molecular still (tested with mercury) the substance did not distil or sublime; there was no melting point, and the solid merely darkened. Color, yellow to orange-yellow, perhaps due to free thiocyanic acid.

Antimony Cyanates

Preparation.—Twenty-seven grams of distilled antimony trichloride was dissolved in 150 ml. of pure benzene, and 60 g. (an excess) of powdered silver cyanate was added,

with shaking. After ten minutes on a steam-bath the reaction started, with extremely vigorous boiling of the solvent. After thirty minutes, with shaking and addition of more benzene, the solution was filtered hot. Some $\text{Sb}(\text{NCO})_3$ deposited as needles from the solution upon cooling. Three hundred ml. of hot benzene was used in washing the solid mixture, but the major fraction of the antimony isocyanate remained undissolved; the solubility of this isocyanate is much less than (2 g./100 ml.) of benzene at 30°. Upon careful evaporation of all the benzene, the solid was transferred to a molecular still, and partially sublimed— $P = 0.001$ mm. approximately; temperatures, upper bath -78° , lower bath 175° ; distance between surfaces about 25 mm.

Analysis for antimony (*cf.* arsenic isocyanate): found 48.9, 49.2%; calculated 49.13% Sb.

Properties.—The color was pure white; small crystals in sublimation; larger crystals from a benzene solution. The vapor pressure was roughly 0.002 mm. at 125° . At 160° this $\text{Sb}(\text{NCO})_3$ isomerizes, with considerable swelling, to $\text{Sb}(\text{OCN})_3$, even with gradual elevation of temperature. The calculated m. p., 196° , is above the isomerization point.

Non-volatile Form; Antimony Cyanate.—The outstanding features of the supposed $\text{Sb}(\text{OCN})_3$ are: its non-volatility at 0.001 mm.; the swelling at 160° , during its production from $\text{Sb}(\text{NCO})_3$; lastly, evolution of gas when the cyanate is hydrolyzed in water.

Discussion of Results

Outside of the fifth group of the periodic table, the only available boiling points were $\text{Si}(\text{SCN})_4$, b. p. 314.2° ,⁴ $\text{Si}(\text{NCO})_4$, b. p. 185.6° ,¹ and $\text{Si}(\text{OCN})_4$, b. p. 247.2° .¹ The cyanate and isocyanate isomers were obtained in a definite ratio in several experiments; no evidence has been obtained indicating transformation of one isomer into the other.

In the fifth group definite trends have been observed. Isomeric changes are: $\text{P}(\text{NCO})_3 \xrightleftharpoons[100^\circ]{\text{slowly}} \text{P}(\text{OCN})_3$.¹ As shown above, $\text{PO}(\text{NCO})_3 \xrightarrow{\text{heat}} \text{PO}(\text{OCN})_3$. $\text{As}(\text{NCO})_3 \xrightarrow{\text{heat}} \text{As}(\text{OCN})_3$. $\text{Sb}(\text{NCO})_3 \xrightarrow{\text{heat}} \text{Sb}(\text{OCN})_3$. The evidence with the thiocyanates is not so clear-cut. Miquel³ said his $\text{P}(\text{SCN})_3$ boiled between 260 and 270° (average 265); Dixon² described $\text{P}(\text{SCN})_3$ as follows, "A reddish-yellow, clear, dense oil . . . at 170° . . . suddenly changed to a sticky black solid which presently became hard and brittle." $\text{PO}(\text{SCN})_3$ shows no marked isomeric changes. The behavior of $\text{As}(\text{SCN})_3$ seems intermediate, between $\text{P}(\text{SCN})_3$ and $\text{PO}(\text{SCN})_3$; upon expulsion of the last trace of solvent at reduced pressure, the liquid turned into a yellowish solid which was not volatile—not even in a molecular still.

(3) Miquel, *Ann. chim. phys.*, [V] **II**, 343 (1877).

(4) Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).

Regularity of Boiling Points.—A comparison of the boiling points of isocyanates with those of the corresponding chlorides shows interesting regularities. The difference between the boiling points of PCl_3 and $\text{P}(\text{NCO})_3$ divided by the number of halogenoid groups is $31.9^\circ - (169.3 - 73.5)/3$. When $\text{PO}(\text{NCO})_3$, $\text{As}(\text{NCO})_3$, and $\text{Si}(\text{NCO})_4$ are included, the average increment is 31.0° . The only volatile cyanate, $\text{Si}(\text{OCN})_4$, yields a higher increment, 47.4° .

Upon comparing the thiocyanate series with the corresponding chlorides, the increment is also found identical; $\text{P}(\text{SCN})_3$, $\text{PO}(\text{SCN})_3$, and $\text{Si}(\text{SCN})_4$ yield an average increment of 64.1° . All of these three thiocyanates have been shown to be thiocyanates, not isothiocyanates.

Further work in this field is planned. The author is much indebted to Professor George S.

Forbes, of this Laboratory, for valuable suggestions during the experimental work.

Summary

1. Phosphoryl isocyanate, $\text{PO}(\text{NCO})_3$, arsenic isocyanate, $\text{As}(\text{NCO})_3$, and antimony isocyanate, $\text{Sb}(\text{NCO})_3$, have been prepared by the action of silver (iso)cyanate with the appropriate chloride.

2. Thermal transformations of these volatile isocyanates into the corresponding non-volatile cyanates have been observed.

3. Phosphoryl thiocyanate has been isolated; arsenic thiocyanate, provisionally reported by Miquel, has been found non-volatile.

4. Various physical properties have been investigated quantitatively and an apparent regularity of boiling points has been observed.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 24, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Potassium Oxalatostannate¹

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Previous workers³ prepared and studied the complex oxalatostannates. Pechard^{3b} claimed to have isolated a complex oxalatostannic acid, but he made no investigation of it. Hausmann and Löwenthal^{3a} and Rosenheim and Platsch^{3c} found that such an acid of constant composition could not be obtained.

Pechard prepared a potassium salt by dissolving stannic acid in potassium bioxalate solution and reported a formula $\text{K}_2\text{SnO}(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$. Rosenheim and Platsch repeated Pechard's work but got entirely different results and reported a formula $\text{K}_6\text{Sn}_2(\text{C}_2\text{O}_4)_7 \cdot 5\text{H}_2\text{O}$. They state that the usual qualitative reactions for stannic tin and for oxalic acid are completely concealed and attribute this to the formation of a complex.

In connection with some proposed studies on oxalatothiostannates, further studies were made on the oxalatostannates.

Experimental

Preparation of Oxalatostannates.—The previous use of stannic acid in preparing solutions of oxalatostannates was

(1) From a dissertation submitted by Taft Y. Toribara in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, 1942.

(2) Florence Fenwick Memorial Fellow, 1939–1942.

(3) (a) Hausmann and Löwenthal, *Ann.*, **89**, 104 (1854); (b) Pechard, *Compt. rend.*, **116**, 1513 (1893); (c) Rosenheim and Platsch, *Z. anorg. Chem.*, **20**, 308 (1899).

tedious as well as undesirable because of the introduction of adsorbed impurities. For this reason a scheme was devised for preparing a solution of stannic tin in excess of oxalic acid only. Attempts to isolate an oxalatostannic acid proved unsuccessful as previous workers had found. The potassium salt was prepared and studied.

A mixture of 25 g. of metallic tin (30-mesh) and 125 g. of oxalic acid in 800 ml. of distilled water was cooled in an ice-salt-bath to about 5° . With continuous mechanical stirring, 150 ml. of 30% hydrogen peroxide (superoxol) was gradually added, and the reaction mixture was kept cool until all the tin had dissolved. Such a procedure required six hours or more. The excess of hydrogen peroxide was decomposed by adding 40 mg. of finely divided platinum black, and the solution was kept cool in an ice-salt bath during this procedure to prevent hydrolysis of the tin. The platinum was removed by filtration and the filtrate was the desired solution of oxalatostannic acid in excess of oxalic acid.

To prepare the potassium salt, the solution was analyzed for total oxalate and for tin. Allowing two moles of oxalate per mole of tin, the excess oxalic acid was neutralized by adding the calculated quantity of solid potassium bicarbonate. The solution was cooled to 0° , and the solid was filtered off. To recrystallize the salt obtained, it was dissolved in the smallest amount of water at 60° , allowed to cool to room temperature and then cooled to 0° . This salt was found to be very stable, and the air-dried solid gave a very definite composition, $\text{K}_6\text{Sn}_2(\text{C}_2\text{O}_4)_7 \cdot 4\text{H}_2\text{O}$. The potassium was determined gravimetrically as the perchlorate after first removing the tin by dropping hydrobromic acid into a boiling perchloric acid solution. The tin was determined gravimetrically as stannic oxide, using