

*m*-, and *p*-nitrophenolate ions, and is, at the same time, in harmony with the known facts concern-

ing *m*-quinone and the oxidation of *m*-diphenols. CAMBRIDGE, MASS. RECEIVED DECEMBER 28, 1939

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## Cyanates of Silicon, Phosphorus and Boron. Instability of Certain Ternary Boron Compounds

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Reynolds<sup>1</sup> prepared stable silicon thiocyanate (b. p. 314°) from silicon tetrachloride and lead thiocyanate in benzene. Two years later, Cock- sedge,<sup>2</sup> upon treating boron bromide with silver thiocyanate, obtained boron thiocyanate as a white crystalline solid which grew dark even at 100°. Both offered some evidence that sulfur, not nitrogen, was linked to the non-metallic element. Dixon<sup>3</sup> reported the isolation of phosphorous thiocyanate from lead thiocyanate and phosphorus trichloride in commercial benzene as "a reddish-yellow, clear, dense oil which gave the reactions for thiocyanate, thiocarbimide and phosphorus." At 170° the contents of the flask "suddenly changed, without evolution of gas, to a sticky black solid which presently became hard and brittle." Dixon thought that this might be a polymer of P(NCS)<sub>3</sub>, but was unable to substantiate his opinion.

It occurred to us to inquire whether these weakly electronegative elements would form stable cyanates, or isocyanates or both. Preparations were undertaken to obtain evidence bearing upon this issue.

### Silicon Isocyanate and Cyanate

**Preparation.**—Eighty grams of silicon chloride was added with vigorous shaking, over a period of fifteen minutes to 250 cc. of pure benzene in which 290 g. of finely powdered silver (iso)cyanate was suspended. The flask was then heated on the steam-bath for half an hour. After filtration, and several washings with benzene, the solvent was distilled off at atmospheric pressure. The yield of crude liquid product, 72 g., was 78% referred to cyanate. Potassium and lead cyanates were much less reactive and led to much smaller yields even after forty hours of refluxing. A second preparation, starting with excess of silicon chloride, afforded a yield of 86%. After expulsion of silicon tetrachloride and benzene, the colorless liquid product was distilled under 25 mm. pressure. The boiling point rose sharply at the end, and the residue, a very pale yellow liquid, was found to be 2.5% of the whole.

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

(2) Cockledge, *ibid.*, **93**, 2177 (1908).

(3) Dixon, *ibid.*, **79**, 541 (1901).

*Anal.* Weighed portions of each fraction were converted into silica by hydrolysis, evaporation and ignition to constant weight all in the same crucible. The results follow.

Fraction of b. p. 185.6°, silicon found 14.22, 14.27, 14.46, 14.47%, average 14.35%.

Fraction of b. p. 247.2°, silicon found 14.06 and 14.56%, average 14.31%.

Calculated for Si(NCO)<sub>4</sub> and Si(OCN)<sub>4</sub>, 14.32%.

The molecular weight of each fraction was determined in Dumas bulbs of about 50 cc. capacity, with the usual precautions.

186° fraction, mol. wt. found 202.5, 205.7, average 204.1.

247° fraction, mol. wt. found 211.9.

Calculated for Si(NCO)<sub>4</sub> and Si(OCN)<sub>4</sub>, 196.1.

In addition, the molecular weight of the 186° fraction was determined by the freezing point method in benzene solution to be 204.1 and 194.4, average 199.2. Not enough of the higher boiling fraction for this determination remained.

**Properties.**—The boiling points were measured at various pressures by a dynamic method described, among others, by Mack and France.<sup>4</sup> Rubber connections were avoided by fused joints. The thermometers for these and other definitive measurements were standardized in the same apparatus with water, aniline and benzoic acid as primary standards, also with bromobenzene and benzoyl chloride. The plot of log<sub>10</sub> *p* (mm.) for each liquid, against 1/*T* was a satisfactory straight line, and the logarithmic equations predicted the data within three millimeters, assuming the correctness of the temperatures. Densities at 20° were determined only by weighing the contents of a pipet. The index of refraction (white light), also at 20°, was measured with an

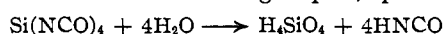
TABLE I

	Si(NCO) <sub>4</sub>	Si(OCN) <sub>4</sub>
B. p., °C., 760 mm.	185.6 ± 0.3	247.2 ± 0.5
M. p., °C.	26.0 ± 0.5	34.5 ± 0.5
log <sub>10</sub> <i>p</i> (mm.)	9.0198–2816/ <i>T</i>	9.8211–3611/ <i>T</i>
λ <sub>v</sub> , cal.	12,900	16,500
λ <sub>v</sub> / <i>T</i> , cal./°	26.5	31.7
<i>d</i> , g./cc.	1.409, 1.413 ± 0.005	1.414 ± 0.005
<i>n</i>	1.4610 ± 0.0003	1.4646 ± 0.0003

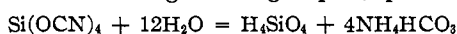
(4) Mack and France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1934, p. 77.

Abbe refractometer with thermostated prism. Table I summarizes the data obtained.

The above identification of the two silicon cyanates rested mainly upon analogies with ethyl isocyanate and cyanate, respectively. The structures of the latter were established by Anschütz<sup>5</sup> and Ponomareff<sup>6</sup> who showed that hydrolysis of the first yielded diethylurea and carbon dioxide, hydrolysis of the second urethan. The difference between their boiling points, 60 and 160°, respectively, agrees with that of the two silicon cyanates. Further evidence was available from their respective behavior when hydrolyzed. The reaction of the low-boiling liquid, presumably



was vigorous, and the silica was largely coagulated due to its formation in acid solution. But the reaction of the high-boiling liquid, presumably



was slow, and silica was obtained in the form of a sol, which proved extremely hard to dehydrate.

The prospect of a decisive proof of the structures of our silicon cyanates, as well as those of boron and phosphorus by purely chemical methods, appears less bright than by Raman spectra or electron diffraction data. It is hoped that such studies may be undertaken, at a later date, in this Laboratory.

### Phosphorous Isocyanate

**Preparation.**—Ninety grams of phosphorus trichloride reacted with 230 g. of silver (iso)cyanate in 300 cc. of warm benzene. After filtration and expulsion of the solvent, 62 g. of liquid remained, nearly 80% of the theoretical yield based on cyanate. After several distillations a colorless liquid was obtained boiling at 167° (uncorrected) under 755 mm. There was a higher boiling fraction of about 2% which decomposed yielding a dark residue. This residue, observed in each of two runs, was hydrolyzed by water.

**Anal.**—The redistilled product contained no chloride. Weighed samples were hydrolyzed to phosphorous and (iso)cyanic acids. A known volume of standard iodine solution was added, and the solution made about 3 *N* in hydrochloric acid. After an hour on the steam-bath, the oxidation of phosphorous to phosphoric acid was assumed to be complete. The excess of iodine was then titrated with standard thiosulfate. Phosphorus found, 20.02 and 20.11%. Calculated, 19.75%. The molecular weight of the vapor, by the Dumas method, was 159.0 and 158.6. Calculated for  $\text{P}(\text{NCO})_3$ , 157.1.

**Properties.**—Our data for the more important physical properties were as follows: boiling point at 760 mm.,  $169.3 \pm 0.3^\circ$ ; melting point,

$-2 \pm 0.5^\circ$ ; vapor pressure,  $\log_{10} p$  (mm.) =  $8.7455 - 2595/T$ ;  $\lambda_v = 11,900$  cal.;  $\lambda_v/T = 26.8$  cal./deg.; density 1.439 g./cc.; refractive index (white light)  $n$ , 1.5352.

Our identification of the product as isocyanate rests largely upon its normal boiling point,  $169.3^\circ$ , which is even lower than that of phosphorus tribromide,  $172.9^\circ$ , and far below that which would be predicted for a normal cyanate, judging from corresponding ethyl and silicon compounds. The Trouton constant, also, agrees with that of silicon isocyanate in a clean-cut fashion.

The purest product displayed some unexpected phase relationships. The distillate boiling at  $169.3^\circ$  stood for two weeks at room temperature without visible change. Upon supercooling it to  $-20^\circ$ , a white solid appeared having a melting point of  $-2^\circ$ . The resulting liquid, held at room temperature for three days, turned into a white solid, melting at about  $80^\circ$ , and insoluble in benzene, ether, chloroform and carbon tetrachloride. Sidgwick<sup>7</sup> has summarized various investigations upon polymers of cyanic acid. Cyanuric acid, soluble in ordinary solvents, can be converted to cyanic acid, which repolymerizes to cyanelide, a solid insoluble in the same solvents. Without attempting to press the analogy too far, we consider the behavior of our phosphorous isocyanate rather similar to the above. Our insoluble solid melting at  $80^\circ$  yielded a liquid boiling at  $169.3^\circ$  like the original liquid, but another sample held at room temperature yielded once more the supposed polymer, melting this time at  $95^\circ$ . Possibly the polymerization was more nearly complete than in the solid melting at  $80^\circ$ .

### Boron Cyanate

**Preparation.**—Forty grams of silver (iso)cyanate, 8 g. of boron bromide and 125 cc. of warm benzene were shaken in a flask. The resulting solution contained about one-quarter of the expected boron cyanate and extraction of the solid residue with benzene removed but little more. A large box was provided with a glass cover, a built-in steam coil, and holes in the sides with wristlets having elastic bands to fit snugly over the operator's gloves. Air was expelled by tank nitrogen, and a slow current maintained during filtration, evaporation to a small volume, drying of the crystals, and sampling. Hydrolysis of the solid was negligible under these conditions.

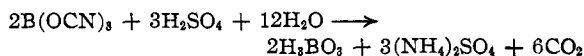
**Anal.** The white solid decomposed with evolution of carbon dioxide in water and in dilute sulfuric acid, thus

(7) Sidgwick, "Organic Chemistry of Nitrogen," revised by Taylor and Baker, Clarendon Press, Oxford, 1937, pp. 322-326 and 331.

(5) Anschütz, *Ann.*, **359**, 210 (1908).

(6) Ponomareff, *Ber.*, **15**, 513 (1882).

indicating presence of cyanate. No bromide was detected in the resulting solution. Four samples, ranging from 0.1071 to 0.3592 g., were weighed under dry nitrogen and hydrolyzed in dilute sulfuric acid.



After expulsion of carbon dioxide, standard sodium hydroxide was added to a methyl red end-point. Enough mannite was added to yield a 10% solution, and titration followed to a phenolphthalein end-point. In a blank experiment with an equal weight and concentration of ammonium sulfate the proper correction for its buffering action was evaluated. Boron found was 8.12, 7.94, 7.87 and 8.05%, average 7.99%; the calculated value is 7.91%.

**Properties.**—Boron cyanate, like boron thiocyanate, was isolated from benzene in tiny crystals. Its solubility in benzene, ether, chloroform or dioxane is roughly 2 g. per 100 cc. Anhydrous ethanol dissolves it with rapid decomposition. Bromine is unreactive at 25° and at 200°. An attempt was made to sublime it in a good vacuum, with cautious heating, but the substance merely became brown to black in color. The fact that our product had no melting point, and could not even be sublimed, suggested that its structure was analogous to that of boron thiocyanate as established by Cocksedge.<sup>2</sup>

### Instability of Certain Ternary Boron Compounds

Before preparing the cyanates, efforts were made to obtain boron chlorobromides, analogous to the silicon chlorobromides previously studied by one of us.<sup>8</sup> Besson<sup>9</sup> had reported the existence of boron bromoiodides, but his evidence that the scanty products were single definite compounds left much to be desired. On the other hand, Poggiale<sup>10</sup> obtained only boron chloride from boron bromide treated with chlorine. Gustavson<sup>11</sup> and Tarible<sup>12</sup> employing carbon tetrachloride and arsenic trichloride, respectively, reported the same outcome. Amorphous boron, from boric oxide and magnesium, was treated with bromine vapor at 800°. The resulting boron bromide was purified by distillation. We employed a three-necked flask with stirrer, separatory funnel and a column leading to a condenser. In successive experiments boron bromide was treated separately with sulfur monochloride, stannic chloride and titanium tetrachloride. The vapors, upon

leaving the heated zone, were cooled by dry ice. Sulfur monochloride yielded only boron chloride mixed with unchanged boron bromide, and the flask contained sulfur monobromide. Titanium tetrachloride and stannic chloride reacted quantitatively with boron bromide. Next, hydrogen chloride was bubbled through boron bromide at 65° and the mixed vapors passed through a tube heated to 800° over a length of 70 cm., but boron bromide and chloride, only, were recovered. It was hoped that silicon dichlorodibromide might yield boron dichlorobromide, but boron trichloride was the only low-boiling product obtained at 800°, with a yield of 10%.

In addition, simple products only were obtained from the following reactions: (1) boron with mixed chlorine and oxygen, the temperature of the reaction zone being gradually lowered from 800 to 650°; (2) boron with mixed chlorine and bromine at 800°; (3) boron bromide and oxygen at 800°; and (4) boron bromide and antimony trifluoride at 90°.

### Summary

1. Silver (iso)cyanate reacts with silicon tetrachloride, phosphorus trichloride and boron bromide in benzene far more completely than does potassium cyanate or lead cyanate.

2. Ninety-eight per cent. of the product obtained from silicon tetrachloride appears to be  $\text{Si}(\text{NCO})_4$ , m. p. 26.0° and b. p. 185.6°; the remainder was  $\text{Si}(\text{OCN})_4$ , m. p. 34.5° and b. p. 247.2°. Our identification rests mainly upon analogies with ethyl isocyanate and cyanate. Various physical properties were quantitatively investigated.

3. Phosphorus trichloride yielded  $\text{P}(\text{NCO})_3$  as the only volatile product, m. p. -2.0°, b. p. 169.3°. Samples once frozen, on standing at room temperature, were converted into a solid insoluble in ordinary organic solvents which reverted to the original (soluble) liquid on heating.

4. Boron trichloride yielded a white solid of low solubility which decomposed on moderate heating. Its analysis, as well as its properties, indicated that it was  $\text{B}(\text{OCN})_3$ .

5. Boron chlorobromides, fluorobromides, oxychloride and oxybromide were not obtained in a series of experiments in which both reactants and temperatures were widely varied.

(8) Schumb and Anderson, *THIS JOURNAL*, **59**, 651 (1937).

(9) Besson, *Compt. rend.*, **112**, 1002 (1891).

(10) Poggiale, *ibid.*, **22**, 124 (1848).

(11) Gustavson, *Ann. chim. phys.* (5) **2**, 228 (1874).

(12) Tarible, *Compt. rend.*, **132**, 207 (1901).