



activated complex. The concentration of deuterium in the alkylsulfuric acid and the relative rates of racemization and deuteration require the rate of interconversion of alcohol and alkene at equilibrium to be smaller than the rates of the other two interconversions.

Any mechanism in which butylene is an intermediate, is excluded by the but partial racemization. While *s*-butylsulfuric acid is not so excluded, it is difficult to avoid similar intermediates in the dehydration and hydrolysis reactions unless one allows the unimolecular decomposition of the alkylsulfuric acid to butylene.

Summary

1. The action of sulfuric acid- d_2 on optically active *s*-butyl alcohol results in the introduction of deuterium on the carbon skeleton concurrently with the racemization of the alcohol.

2. The *s*-butylsulfuric acid present in the reaction mixture is both more racemized and further exchanged than the alcohol present as such.

3. The velocity of the racemization reaction is about the same in heavy sulfuric acid as in ordinary acid. Its rate is several times greater than that of the exchange reaction.

4. The formation of *s*-butylsulfuric acid from *s*-butyl alcohol by reaction with (a) sulfuric acid, (b) chlorosulfonic acid, and (c) sulfur trioxide in solution in dioxane proceeds without change in configuration.

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Since barium *s*-butyl sulfate does not hydrolyze in neutral solution, the un-ionized acid, not the alkylsulfate ion, must be made the reacting species. This is not unreasonable, since otherwise in the formation of the carbonium ion a doubly negatively charged ion would have to separate from a positive ion. With the un-ionized acid, the separation is of singly charged ions.

The hydrolysis of barium *s*-butyl sulfate apparently resembles that of the barium salt of the ethylsulfuric acid. Drushel and Linhart⁸ have shown that this salt hydrolyzes extremely slowly in water alone but that in dil. hydrochloric acid the reaction proceeds at a convenient rate. The rate in the more dilute solutions is nearly proportional to the first powers of the concentrations of the salt and of the hydrogen ion.

Since but partial racemization results from the intertransformations of alcohol and alkylsulfuric acid, the life of the carbonium ion must be assumed slight. It would probably be more satisfactory to express the mechanism in terms of an

(8) Drushel and Linhart, *Am. J. Sci.*, **32**, 51 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Chlorothiocyanates of Phosphorus and Silicon. Phosphorus Chloro(iso)cyanate

BY HERBERT H. ANDERSON

Previous papers in this series dealing with the pseudohalide derivatives of elements of the fourth and fifth groups have described the thiocyanates and the (iso)cyanates of phosphorus and silicon,^{1,2} the chloroisocyanates of silicon,³ and related compounds. The present investigation deals with the chloro(iso)cyanates of phosphorus and the chlorothiocyanates of silicon and phosphorus, prepared by the action of silver (iso)cyanate or silver thiocyanate with the appropriate chlorides in benzene solution, or in carbon disulfide solution. The pres-

ent compounds are believed to include the first inorganic mixed halides containing thiocyanate as a constituent.

Silicon Trichlorothiocyanate.—The optimum yield of SiCl_3SCN was obtained using a ratio of 0.54 mole of SiCl_4 to 0.60 mole of AgSCN ; the silver salt was added in six separate portions, with intermittent half-hour periods of reflux on a steam-bath. Products were SiCl_3SCN and $\text{Si}(\text{SCN})_4$, in the molar ratio 0.33 to 0.08. Numerous efforts were made to isolate other products, including the use of low-pressure distillation and fractional freezing. 200 ml. of pure benzene was used as solvent in each run. There was no evidence of $\text{SiCl}_2(\text{SCN})_2$, or $\text{SiCl}(\text{SCN})_3$ at any time.

A small weighed sample of the pure distillate, b. p. 129–130°, after decomposition in absolute alcohol and dilution with water, gave a ratio for SCN^-/Cl^- equal to 1.00/3.00 \pm 0.02, in accordance with theory. Dr. J. J. Lingane of this Laboratory made his electrometric titration

(1) Forbes and Anderson, *THIS JOURNAL*, **63**, 761 (1940); **65**, 2271 (1943). In the latter paper it should have been stated that monomeric sulfur monothiocyanate had previously been prepared by Lecher and Goebel, *Ber.*, **55B**, 1483 (1922).

(2) Anderson, *ibid.*, **64**, 1757 (1942).

(3) Anderson, *ibid.*, **66**, 934 (1944).

apparatus available for this work. One analysis for silicon was made by careful hydrolysis, treatment with nitric acid, evaporation, and ignition. Calcd. for SiCl_2SCN : Si, 14.57; mol. wt. (Dumas), 192.5. Found: Si, 14.52; mol. wt., 200, 194.

Disproportionation.—When a sample of this substance had been heated for twenty hours at 140° , analysis by distillation showed disproportionation into silicon tetrachloride and silicon tetrathiocyanate to the extent of 70%. After five months of standing at room temperature one sample rearranged 34%, another 37%.

The melting points of these and other new substances mentioned below were determined by means of a calibrated toluene thermometer immersed in 3 ml. of the pure liquid in a small tube which was placed in an alcohol-bath in a Dewar flask. The bath temperature was allowed to change slowly with constant stirring, both melting and freezing points being observed. The density was obtained by means of a calibrated 2-ml. bulb with capillary inlet. Results of these measurements and two indices of refraction (Abbe refractometer, white light) are collected in Table I.

TABLE I
PROPERTIES OF NEW COMPOUNDS

Compound	B. p., °C.	M. p., °C.	n_D^{20}	Density
$\text{SiCl}_2(\text{SCN})$	129.5 ± 0.5	-75 ± 2	1.5091	1.461 (24°)
$\text{POCl}_2(\text{SCN})$	173 ± 1	-55 ± 2	1.5649	1.587 (25°) ^a
$\text{PCl}_2(\text{NCO})$	104.4 ± 0.5	-99 ± 2	...	1.513 (31°)

^a By drainage of pipet.

In addition, dynamic vapor pressure measurements of $\text{SiCl}_2(\text{SCN})$ were made in an all-glass system over the range 67.7° to 129.5° . The values found conform to the equation $\log_{10} p$ (in mm.) = $7.9985 - 2060/T$, with an average error of 1.5%. Also, the heat of vaporization is found to be 9420 cal./mole, and the Trouton constant $\Delta H/T$ to be 23.4 cal./mole/deg.

Phosphoryl Dichlorothiocyante.—Previous experiments using small excesses of POCl_2 with AgSCN had yielded only $\text{PO}(\text{SCN})_2$. However, when 1.45 moles of POCl_2 was mixed with 1.20 moles of AgSCN in 500 ml. of pure, dry benzene and refluxed for forty hours as in the former preparation, 0.28 mole of $\text{POCl}_2(\text{SCN})$ and 0.32 mole of $\text{PO}(\text{SCN})_2$ were obtained. To minimize decomposition of the chlorothiocyante, low-pressure distillation was used; b. p. was 101° at 41 mm., or 122° at 60 mm. No evidence for $\text{POCl}(\text{SCN})_2$ was found in the distillation curves and no further attempts were made to isolate it.

Important physical properties of $\text{POCl}_2(\text{SCN})$ are listed in Table I. These measurements were all made on pure, freshly-redistilled fractions, since rearrangement was of moderate rate even at 25° . Most of the figures are averages of closely agreeing figures obtained on separate samples. After a month at room temperature the melting point was much lower than for pure material and was far from sharp, indicating substantial rearrangement.

Electrometric titration gave a ratio for SCN^-/Cl^- of 1.00/1.99, in close agreement with $\text{POCl}_2(\text{SCN})$. The percentage of sulfur, determined as barium sulfate after treatment with nitric acid, was 18.4 compared to 18.22 calculated for $\text{POCl}_2(\text{SCN})$. Rapid determinations of molecular weight (Dumas) gave 188 and 174, with a calculated value of 176.0 for $\text{POCl}_2(\text{SCN})$.

Phosphorus Dichloroisocyanate.—The success of previous analogous preparations suggested that this compound might be prepared by gradual addition of AgNCO to a large excess of PCl_3 . Even with this procedure rather low yields were obtained in a large number of experiments with either benzene or carbon disulfide as solvent, or without a solvent. The largest amount, 0.13 mole, was obtained by using 0.67 mole of AgNCO and either 1.15 moles of PCl_3 plus 20 ml. of CS_2 , or 2.07 moles of pure PCl_3 . When mixed vapors of PCl_3 and $\text{P}(\text{NCO})_3$ were passed through a tube at 600° , some $\text{PCl}_2(\text{NCO})$ was formed, although most of the cyanate was converted into a solid of undetermined composition. The low yields are due to a

rapid rate of reaction between $\text{PCl}_2(\text{NCO})$ and AgNCO —of greatest importance—and a secondary source of loss, the high volatility of the compounds.

The best fractions of $\text{PCl}_2(\text{NCO})$ could be redistilled without detectable decomposition in a two-hour period at 104.0 – 105.0° . Linear interpolation between the boiling points of PCl_3 and $\text{P}(\text{NCO})_3$ gives a calculated boiling point of 106.8° , in good agreement. Rearrangement of $\text{PCl}_2(\text{NCO})$ was 6% after four months at room temperature, or about 11% after sixteen hours in a sealed tube at 143° . Thus it may be said that $\text{PCl}_2(\text{NCO})$ is rather stable.

Samples were decomposed in absolute ethanol and the products were diluted with water. Chloride was determined by titration with silver nitrate using potassium chromate as indicator. Calcd. for $\text{PCl}_2(\text{NCO})$: Cl, 49.26; mol. wt. (Dumas), 149, 151. Found: Cl, 49.4, 49.3; mol. wt., 144.

Phosphorus Chlorodisocyanate.—In the preparation of $\text{PCl}_2(\text{NCO})$, especially when smaller excesses of PCl_3 were used (Cl/NCO equals 1.5–4.0), substantial fractions (ca. 0.05 mole) centering about a boiling point of 135° were obtained, indicating $\text{PCl}(\text{NCO})_2$. This material rearranged into $\text{PCl}_2(\text{NCO})$ and $\text{P}(\text{NCO})_3$, so severely at 135° that it is doubtful whether it can ever be prepared in a pure state. However, there is slight hope that distillation at 0.2 mm. might solve the problem.

Stability of $\text{PO}(\text{NCO})_2$ and $\text{PS}(\text{NCO})_2$.—These previously prepared compounds have now been observed after a considerable time at room temperature. Phosphoryl (iso)cyanate³ has been standing for twenty-nine months and thiophosphoryl (iso)cyanate¹ for fourteen months. Both are changing into the non-volatile yellow solid isomers; the thiophosphoryl cyanate at an apparently faster rate.

Discussion

It can be seen from the above results that one thiocyanate group is probably the limit consistent with stability; one (SCN) raises the boiling point 64° on the average²; two would mean 128° over the corresponding chloride, and this is too high a boiling point to escape a rearrangement of the groups attached to the central atom. For an adequate discussion of the principle involved, see a previous report.⁴ In the case of $\text{PCl}(\text{NCO})_2$, a boiling point of 135° is not far from 138.1° , the boiling point calculated by interpolation, and the high rate of rearrangement is undoubtedly due to a structural strain, or heterogeneity within the molecule, present in PX_3 mixed halides.

A sufficient number of the pseudo-halogen derivatives have now been studied in this and previous reports to permit some generalizations regarding their stabilities and ease of preparation. A number of these conclusions are listed and examples given in the following paragraphs.

1. Chlorothiocyanates are more easily prepared than the corresponding chloroisocyanates but are less stable against rearrangement. $\text{SiCl}_2(\text{SCN})$ is prepared with higher yield than is $\text{SiCl}_2(\text{NCO})_2$, but its rearrangement in four months at room temperature is about 35%, compared to 2–3% at most for the cyanate analog. Ease of preparation of $\text{PCl}_2(\text{NCO})$ compares favorably with two attempts to make $\text{PCl}_2(\text{SCN})$, both of which failed.

2. Mixed halides or mixed pseudohalides of silicon are more stable than those of trivalent

(4) Forbes and Anderson, THIS JOURNAL, 66, 931 (1944).

phosphorus. An array of easily prepared $\text{SiCl}_3(\text{NCO})$, $\text{SiCl}_2(\text{NCO})_2$, $\text{SiCl}(\text{NCO})_3$, and $\text{SiCl}_3(\text{SCN})$ compare with $\text{PCl}_2(\text{NCO})$ alone. Silicon fluorobromides are all stable,⁵ while PF_2Br and PBr_2 were somewhat unstable.⁶

3. Phosphoryl and thiophosphoryl mixed halides are more stable than those of trivalent phosphorus. Booth and Seabright concluded this also⁷ on the basis of fluorohalides. $\text{POCl}_2(\text{SCN})$ or POCl_2Br versus apparently unstable $\text{PCl}_2(\text{SCN})$ or PCl_2Br .⁸

The author is indebted to Professor G. S.

(5) Schumb and Anderson, *THIS JOURNAL*, **58**, 994 (1936).

(6) Booth and Frary, *ibid.*, **61**, 2934 (1939).

(7) Booth and Seabright, *ibid.*, **65**, 1834 (1943), and references therein.

(8) See, however, T. Mitobedski, *Chem. Abstracts*, **27**, 474 (1933).

Forbes of this Laboratory for helpful suggestions. Other investigations are under way.

Summary

1. Two new chlorothiocyanates, $\text{SiCl}_3(\text{SCN})$, b. p. 129.5° , and $\text{POCl}_2(\text{SCN})$, b. p. 173° , have been prepared; one new chloro(iso)cyanate, $\text{PCl}_2(\text{NCO})$, b. p. 104.4° , also has been synthesized. Their chief physical properties have been determined. $\text{PCl}(\text{NCO})_2$ was also indicated, but rearranged too rapidly for feasible isolation.

2. $\text{PCl}_2(\text{NCO})$ is fairly stable at 25° , whereas $\text{PCl}(\text{NCO})_2$ is considerably less stable.

3. A comparison of the stability of various mixed halides of silicon and phosphorus is presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Electrical Conductivity of Thallous Chloride Solutions of Ethylene Glycol-Water

BY A. B. GARRETT AND SIMON J. VELLENGA

The purpose of this investigation was to study the equilibria of thallous chloride in ethylene glycol-water solutions from electrical conductivity data. This supplements a study of these equilibria by e. m. f. and solubility data in this solvent mixture¹ and in alcohol-water mixtures² by solubility measurements. A method for determining dissociation constants of thallous chloride was developed in that study.³

The dissociation constants in ethylene glycol-water have a minimum value at 60% glycol.¹ This unpredicted effect required further investigation; it was deemed desirable to determine the dissociation constants of thallous chloride by the conductance method.

Experimental

1. **Ethylene Glycol.**—The ethylene glycol was purified by the method of Smyth and Walls¹ in which the ethylene glycol was distilled three times under reduced pressure using the middle fraction of the distillate each time. The boiling point under the reduced pressure was about 90° . The first distillate was shaken with anhydrous sodium sulfate and the second and third distillates were kept under nitrogen in glass-stoppered bottles. In the distillation under reduced pressure a stream of purified nitrogen was passed through the ethylene glycol in the still by means of a capillary to prevent bumping.

2. **Thallous Chloride.**—Thallous chloride was prepared by means of the method of Hogge and Garrett.²

3. **Hydrochloric Acid.**—Grasselli c. p. grade hydrochloric acid was distilled in an all-glass still; the middle fraction was taken for use.

The conductances of the samples were determined by means of the Jones electrolytic conductance bridge. The oscillator used was an 8-A oscillator, manufactured by the Western Electric Company. It was adjusted to give a frequency of 2400 cycles. The conductivity cells incor-

porated the Jones and Bollinger⁴ feature which has the filling tubes as far apart as possible. The cells were suspended in an oil thermostat bath at $25 \pm 0.005^\circ$ by a Thyatron controlled circuit. The ethylene glycol-water samples and the thallous chloride solvent mixtures were all made up by weight. All work was done under nitrogen; the samples were transferred to the cells under nitrogen pressure.

Cells were rinsed at least seven times with the solution to be used before they were filled. The resistances of the samples were determined after temperature equilibrium had been reached. This required approximately an hour. The weight molality was transformed into volume molarity by use of the density of the solvent.⁵

TABLE I

ELECTRICAL CONDUCTANCE OF THALLOUS CHLORIDE IN WATER

	Molarity, <i>m</i>	Δ_0
A. Data from Bray and Winninghoff, <i>THIS JOURNAL</i> , 33 , 1663 (1911); Δ = legend		
	0.00507	143.10
	.00604	142.25
	.01000	139.00
	.01108	138.35
	.01607	135.4
B. Data from "International Critical Tables," 6 , 232, 257; \circ = legend		
	0.002	146 (extrapolated)
	.005	142.9
	.010	138.8
	.0167	135.3
C. Data from this Research; \times = legend		
	0.00150	148.40
	.00750	141.13
	.01501	136.03

(1) Black and Garrett, *THIS JOURNAL*, **65**, 862 (1943).

(2) Hogge and Garrett, *ibid.*, **68**, 1089 (1941).

(3) Smyth and Walls, *ibid.*, **58**, 2115 (1931).

(4) Jones and Bollinger, *ibid.*, **53**, 411 (1931).

(5) Black. Ph. D. Thesis, The Ohio State University, 1942.