is soluble in germanium tetrachloride[19]; however, the formula $Ge_2O(NCO)_6$ must be conceded as possible. Because of uncertainties due to the difficultly removable cyanuric acid, a polymer of isocyanic acid, and also because of increased ease of hydrolysis, molecular weight determinations were not undertaken on the limited amount of solution available; under *ideal* circumstances the molecular weight would differentiate between $[GeO(NCO)_2]_n$ and $Ge_2O(NCO)_{6m}$ and also give a value for n, perhaps 3 or 4.

Discussion

(1) An inspection of the series from germanium tetraisocyanate to tetraethylgermanium indicates: a smooth progression in densities; a smooth progression in refractive indices; good agreement with the calculated molar refractions; three melting points of ternary compounds which are nearly the same; two boiling points that are almost identical, and two more only four degrees apart.

(2) These striking boiling points are on the average only 5.6° lower than values which may be calculated from the boiling points of the corresponding chlorides, using the increment method of adding 30° per isocyanate group[3]: triethylgermanium isocyanate, 205.9°; diethylgermanium diisocyanate, 232.9°; ethylgermanium triisocyanate, 230.0°. A variation in the increment value itself is plausible: 30.2° for the tetraisocyanate; 28.5° for the triisocyanate; 26.6° for the diisocyanate; 24.5° for the monoisocyanate.

(3) It may be possible to prepare germanium tetraisothiocyanate by some method other than from silver isothiocyanate and tetrachlorogermane; the lack of success of this reaction is no undeniable proof of the non-existence of germanium tetraisothiocyanate.

(4) The previously detected impurity in crude germanium tetraisocyanate[2] is either $[GeO(NCO)_2]_n$ or, less probably, $Ge_2O(NCO)_6$—rather than either $Ge(OCN)_4$ or $Ge(NCO)_2$. Such a finding is in keeping with the *lone existence*[1] of $Si(OCN)_4$ in contrast to numerous volatile inorganic isocyanates.

Summary

1. Each of the three ethylchlorogermanes reacted with silver isocyanate to yield the (new) corresponding pseudo halide. Triethylgermanium isocyanate, $(C_2H_5)_3Ge(NCO)$, boils at 200.4°; diethylgermanium diisocyanate, $(C_2H_5)_2Ge(NCO)_2$, boils at 226.0°; ethylgermanium triisocyanate, $(C_2H_5)Ge(NCO)_3$, boils at 225.4°. All three compounds are easily purified by distillation under fifty mm. pressure, and their stability against the redistribution reaction is quite a contrast to the very limited stability of germanium chloroisocyanates or chlorobromides. Including the previously known tetraethylgermanium and germanium tetraisocyanate, there is now the first complete series of organogermanium pseudo halides. Vapor pressure equation, densities, melting points and indices of refraction are given; the boiling points are each about 5° lower than the value derived from the boiling point of the corresponding ethylchlorogermane using the increment method.

2. Germanium tetrachloride—herein shown not to react with silver isothiocyanate either in benzene or in nitromethane, a solvent now under investigation—should thus be separable from halides which do react with silver isothiocyanate: silicon tetrachloride, boron trichloride, phosphorus trichloride, sulfur monochloride, sulfuryl chloride and some others. Germanium tetraisocyanate, unlike the tetrachloride or the tetrabromide, reacts readily with methanol or ethanol at room temperature.

3. Careful evaporation of germanium tetraisocyanate has yielded a concentrate of density 1.962, refractive index 1.512 and containing 32.2% germanium. Yellow in color, this is chiefly germanium tetraisocyanate, with a solute of $[GeO(NCO)_2]_n$ or conceivably even $Ge_2O(NCO)_6$. Both the color and method of formation agree with previous findings on silicon oxyisocyanates.

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(19) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, p. 271.

[CONTRIBUTION FROM WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Ethylsilicon Isothiocyanates. Use of Acidimetry without Weighing

BY HERBERT H. ANDERSON

This paper serves a triple purpose: first, an opportunity to establish the usefulness of self-filling, self-adjusting micropipets[1] as a substitute for the weighing of liquids; second, an investigation of the titration of free isothiocyanic acid with alkali, using phenolphthalein as an indicator, in the absence of other acids; third, the synthesis of a complete new series of organosilicon isothiocyanates with an organic nature exceeding that of the methylsilicon isothiocyanates.[2]

Ethylsilicon Isothiocyanates

Preparation.—Ethyltrichlorosilane and diethyldichlorosilane, obtained from tetrachlorosilane and ethylmagnesium bromide, boiled at 98.1–98.5° and 128–130°, respectively, under 771 mm. pressure; the presence of bromine was unimportant since isothiocyanate replaces both chlorine and bromine therein. Triethylchlorosilane, purchased from Anderson Laboratories, Inc., of Adrian, Michigan, was used directly. Twenty grams of each individual ethylchlorosilane and a 30% excess of silver isothiocyanate yielded approximately 85% of the theoretical quantity of the individual ethylsilicon isothiocyanate after the usual thirty minutes at 85°, followed by filtration, washing of the silver salts and evaporation of the benzene. Careful single distillations in an unpacked

(1) Anderson, *Anal. Chem.*, **20**, 1241 (1948), fig. 4.

(2) Anderson, THIS JOURNAL, **69**, 3049 (1947).

TABLE I

PHYSICAL PROPERTIES OF ETHYLSILICON ISOTHIOCYANATES

Compound	B. p., °C.	d^{20}_4	n^{20}, ± 0.0010	R, ml.	Mol. wt. (Dumas) Found	Calcd.
$(C_2H_5)_4Si$	153.7[5]	0.7662[6]	1.4268[6]	48.34[6]	...	144.30
$(C_2H_5)_3Si(NCS)$	210.5 ± 1.5°	0.934	1.4944	54.06[7]	181	173.32
$(C_2H_5)_2Si(NCS)_2$	245.5 ± 2°	1.089	1.5540	59.54[7]	211	202.33
$(C_2H_5)Si(NCS)_3$	276 ± 2°, 313.0[2]	1.264	1.6195	64.25[7]	240	231.35
$Si(NCS)_4$	314.2[8]	ca. 1.409[9]	.....	70.4[9]	...	260.36

TABLE II

ANALYSES FOR ISOTHIOCYANATE BY ACIDIMETRY

Compound	Volume, microliters at (T) °C.		Density at (T) °C.	Ml. of 0.01949 N alkali used			% NCS Found			Calcd.
$(C_2H_5)Si(NCS)_3$	4.50	(20)	1.264	3.788	3.772		75.4	75.1		75.31
$(C_2H_5)_2Si(NCS)_2$	6.21	(20)	1.089	3.433	3.431		57.5	57.4		57.46
$(C_2H_5)_3Si(NCS)$	15.32	(20.3)	0.934	4.245	4.253		33.59	33.66		33.50
$(CH_3)_2Si(NCS)_2$[2]	5.46	(20)	1.142	3.668	3.674	3.667	66.7	66.9	66.7	66.66
$(C_2H_5O)_3Si(NCS)$[10]	12.65	(20)	1.036	(3.480)[11]	3.032[12]	3.067[12]	...	26.19	26.51	26.24
CH_3COOH, glacial	5.46	(18.4)	1.051	4.881			—99.9% pure—			
	6.29	(22.0)	1.047	5.587			—99.3%— pure			

column 30 cm. long and 4 mm. i. d. yielded center fractions as follows: ethylsilicon triisothiocyanate, b. p. 173.2–174.2° at 38 mm.; diethylsilicon diisothiocyanate, b. p. 73.5–74.5° at 3 mm.; triethylsilicon isothiocyanate, b. p. 128.3–128.9° at 72 mm.

Physical Properties; see Table I.—An Abbe refractometer served for measuring indices of refraction, while a 2-ml. micropycnometer[3] was used for obtaining the densities. All three were colorless liquids of apparently normal viscosity. However, upon cooling ethylsilicon triisothiocyanate to −70°, an extremely viscous liquid resulted which crystallized only when stirred with a small amount of ground-glass, evidently furnishing the surface needed to induce crystallization; thereupon, the m. p. was consistently −30°. Triethylsilicon isothiocyanate has a camphoraceous odor; it hydrolyzes slowly at room temperature and moderately fast at 80°. The diisothiocyanate, triisothiocyanate and tetraisothiocyanate hydrolyze at progressively greater rates.

Titration of Isothiocyanic Acid with Sodium Hydroxide

See Table II.—Gorman and Connell's observation[4] that (iso)thiocyanic acid was a strong acid prompted the titration of this acid after alcoholysis of organosilicon isothiocyanates. Individual solutions of isothiocyanic acid in ethanol were kept only a few minutes, lest there be loss of acidity due either to polymerization or to possible reaction of the acid with alcohol.

A self-filling, self-adjusting micropipet of 0.00546 ml., or 5.46 microliters—mercury calibrated, usually shorter and wider in i. d. than that in Fig. 4, reference 1—served for obtaining a known amount of dimethylsilicon diisothiocyanate, which at 20°, the actual room temperature, has the density 1.142; the sample therefore weighed 6.23_5 mg. Approximately 98% of the contents was delivered in a single operation into one and a half ml. of 95% ethanol—checked previously for neutrality and adjusted if need be—in a 15-ml. round-bottom flask, with use of a 2-ml. syringe; thereupon followed two rinsings with the alcohol in the flask and then two more in a tiny platinum dish holding 0.1 ml., later, dish and contents being placed in the flask holding the main amount. (Some practice is needed for this micromanipulation, and only some micropipets are suitable.) After this, approximately two ml. of freshly-boiled distilled water and two drops of phenolphthalein solution were added. Thereupon, 0.01949 *N* sodium hydroxide solution, made by dissolving sodium metal in a small amount of 95% ethanol and then diluting with freshly-boiled distilled water, served for the titration to the first definite persistent pink color.

Acidimetric results of 66.7, 66.9 and 66.7% NCS were superior to the published argentimetric value of 66.2%,[2] theory requiring 66.66% NCS for $(CH_3)_2Si(NCS)_2$.

Triethoxysilicon isothiocyanate could not be titrated suitably with phenolphthalein as an indicator; the action of 95% ethanol apparently produced some $(C_2H_5O)_3Si(OH)$ which would seem to be a weak acid. However, when methyl red was the indicator, suitable results were attained.

Glacial acetic acid, a commercial C. P. product, was titrated and found to have a purity of 99.6 ± 0.3%. The inclusion of this compound, although not a halide or pseudo halide, served as a demonstration of the general scope of the method.

Discussion

1. It is obvious that halides and pseudo halides containing the Si–O–Si bonding hydrolyze more readily than the simple silane type, Si–Cl or Si–NCO, which in turn hydrolyzes more easily than the organosilicon type such as $(C_2H_5)Si(NCS)_3$. A more extensive comparison will be made at a later date.

2. Numerous variations in the method of titrating the acid, be it isothiocyanic, hydrochloric, isocyanic, or other, are possible. A sample of 20.18 microliters of $(C_2H_5)_3Si(NCS)$ was delivered into 90% of the theoretical equivalence of sodium hydroxide in 95% ethanol, then phenolphthalein solution added, with titration to a perceptible pink; found, 33.59% NCS. This latter method is suitable for compounds which react slowly with water.

A method of dissolving alkylsilicon isocyanates

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(3) Figure 2 in reference 1.

(4) Gorman and Connell, THIS JOURNAL, **69**, 2063 (1947).

(5) As listed by Lewis and Newkirk, *ibid.*, **69**, 701 (1947).

(6) Whitmore, *et al.*, *ibid.*, **68**, 475 (1946).

(7) Calculated molar refractions are 53.85, 59.23 and 64.92 ml..

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

(9) Value obtained, in reference 2, in solution using the law of mixtures.

(10) New compound, data on which is to be published in THIS JOURNAL separately.

(11) Indicator phenolphthalein.

(12) Indicator methyl red, eliminating weak acids.

in excess ethanolic sodium hydroxide, followed by titration of the excess alkalinity, is being given careful study.

3. Investigations now nearing completion concern reactions of the appropriate alkylchlorosilane with silver isocyanate or silver isothiocyanate to yield the following new compounds: $EtSi(NCO)_3$, b. p. 183°; $Et_2Si(NCO)_2$, b. p. 177°; $Et_3Si(NCO)$, b. p. 165°; i-$PrSi(NCO)_3$, b. p. 192°; $PrSi(NCO)_3$, b. p. 198°; i-$PrSi(NCS)_3$, b. p. 279°; $PrSi(NCS)_3$, b. p. 290°.

Titanium tetrachloride and silver isocyanate yield a solid isocyanate which is nearly insoluble in benzene. Titanium tetrachloride and 1,4-dioxane furnish a pale-colored solid addition compound containing approximately 31% Cl, provisionally identified as $TiCl_4.{}_3C_4H_8O_2$, and being investigated further.

Summary

1. Ethylchlorosilanes and silver isothiocyanate reacted to yield (new) liquids: ethylsilicon triisothiocyanate, $(C_2H_5)Si(NCS)_3$, boiling at 276°; diethylsilicon diisothiocyanate, $(C_2H_5)_2Si(NCS)_2$, boiling at 245.5°; and triethylsilicon isothiocyanate, $(C_2H_5)_3Si(NCS)$, boiling at 210.5°. Molar refractions, densities and indices of refraction are given.

2. After treatment of a pure alkylsilicon isothiocyanate with 95% ethanol, the resultant (iso)-thiocyanic acid proves to be easily and accurately titrated with standard sodium hydroxide using phenolphthalein as an indicator. This method in many instances has advantages over previously available procedures for determination of (iso)-thiocyanic acid, which polymerizes, and which is a reducer.

3. Automatic, or self-filling and self-adjusting, micropipets herein of volume 0.004–0.016 ml. have served quite well for exact quantitative analysis of unweighed liquid samples, as now demonstrated. From the mercury-standardized volume of the micropipet and from the known density of the liquid at the observed temperature the weight of the liquid is furnished with accuracy otherwise attainable only with use of a microbalance under extreme precautions.

Further investigation is under way regarding the elimination of weighing analytical samples of liquids through use of such micropipets, and of similar equipment.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Radioactive Tracer Study of Activator Distribution in Infrared Phosphor Systems: Effect of Strontium Oxide[1,2]

BY J. PRENER, R. W. MASON[3] AND R. WARD

It has been shown that strontium oxide has a pronounced effect upon the brightness under stimulation of the infrared-sensitive phosphors SrS (Sm, Eu) $SrCl_2$[4] and SrSe (Sm, Eu) ($SrSO_4$ CaF_2).[5] The brightness of the phosphor SrS (Ce, Sm) $SrCl_2$ invariably decreases with the addition of small amounts of strontium oxide. Lattice constant determinations of strontium sulfide or selenide and strontium oxide that has been fluxed together with strontium chloride at 1000° indicate that the amount of oxide which dissolves in the sulfide and selenide is quite small and lies almost beyond the limits of determination by X-ray diffraction.[6] Inasmuch as quantities of oxide up to several per cent. still have very marked effects upon the luminescent properties of these phosphors, these could not be attributed to any change in the nature of the base material caused by the oxide.

The solubility of strontium oxide in fused strontium chloride[7] at 1000° is sufficiently high so that the quantities of oxide added to the phosphors[4,5] were in all cases insufficient to saturate the fused strontium chloride. It seemed reasonable to suppose that the oxide alters the nature of the flux, and that this might cause a change in the distribution of the rare-earth activators between the solid base material (strontium sulfide or selenide) and the liquid phase (fused strontium chloride plus dissolved strontium oxide and base). A procedure has been described[8] for measuring the distribution of the activators europium, samarium and cerium between the solid strontium sulfide or selenide and liquid strontium chloride. This paper deals with the effect of the addition of strontium oxide upon the distribution of the activators in these systems.

Experimental

(a) Apparatus.—The high temperature filtration method[8] which yielded a partial separation of the solid and

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(1) This work was carried out under Contract NObsr 39045 between the Polytechnic Institute of Brooklyn and the Bureau of Ships.

(2) Abstracted from part of a thesis submitted by Jerome Prener in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(3) Present address: E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(4) K. Stripp and R. Ward, THIS JOURNAL, **70**, 401 (1948).

(5) A. L. Smith, R. S. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).

(6) W. Primak, H. Kaufman and R. Ward, *ibid.*, **70**, 2043 (1948).

(7) Sackur, *Z. physik. Chem.*, **78**, 564 (1912).

(8) R. Mason, C. F. Hiskey and R. Ward, THIS JOURNAL, **71**, 509 (1949).