83.0% NCS, compared with 82.9% calculated for $Si_2O(NCS)_6$.

Molecular weights were determined by depression of the freezing point of camphor. Hydrolysis during the measurements was at least partly responsible for the low values observed, but all these substances were shown to be monomeric. For $Si_2O(NCO)_6$ found 317, calcd. 324; for $Si_3O_2(NCO)_8$ found 417, calcd. 452; for $Si_2O(NCS)_6$ found 390, calcd. 421.

IV. Physical Properties

Hexaisocyanatodisiloxane, a white solid, melted at 44.5° to a clear colorless liquid boiling at 163° at 14 mm., at 190° at 63 mm., or at approximately 260° and one atmosphere—in the last case with decomposition. A specimen originally boiling at 260° and one atmosphere boiled at 235° after a half hour, without formation of silica. This indicates a reaction such as $Si_2O(NCO)_6 \rightarrow Si(NCO)_4 + Si_4O_3(NCO)_{10}$, in general agreement with previous observations on the partial instability of Si_2OCl_6[5] and Si_2OBr_6.[1] The vapor pressure data were not accurate enough for calculation of the heat of vaporization. To determine the molar refraction of the oxyisocyanate as a **liquid** at 20° its melting point was lowered by a sufficient quantity of silicon isocyanate the molar refraction of which is 37.29 ml. From the law of mixtures the molar refraction of the oxyisocyanate is 57.4 ml.

Octoisocyanatotrisiloxane remained a viscous yellowish liquid even at −78°; it boiled at 170° and 2 mm. Direct measurement gave $d^{20}{}_4$ 1.508 and index of refraction 1.4658 in white light, from which a molar refraction of 78.1 ml. results.

Hexaisothiocyanatodisiloxane, a white crystalline solid, melted into a clear and nearly colorless liquid at 120–121°. A specimen previously distilled under low pressure showed an initial boiling point of 347°; in light of the low thermal stability of $Si_2O(NCO)_6$ even this first reading was noted with reservations.

Solubilities.—The oxyisocyanates are apparently completely miscible with acetone and with 1,4-dioxane, but are not completely miscible with carbon disulfide, carbon tetrachloride, benzene and diethyl ether.

Comparison of Molar Refractions.—Stoichiometrically, $Si(NCO)_4 + Si_3O_2(NCO)_8 = 2Si_2O(NCO)_6$ and the numbers of silicon–oxygen bonds are identical but $R_{Si(NCO_4)}$[6] $+ R_{Si_3O_2(NCO)_8} = 37.29 + 78.1$ or 115.4 ml. and $2R_{Si_2O(NCO)_6} = 114.8$. Apparently two linkages to oxygen on a single silicon atom have less effect than two such linkages distributed between two silicon atoms.

Summary

1. The oxyisocyanates and oxyisothiocyanate of silicon exemplify a new type of pseudo halide. As earlier attempts to isolate hexaisocyanatodisilane, $Si_2(NCO)_6$, had been unavailing, the stabilizing effect of the Si–O–Si bonding is apparent. Hexaisocyanatodisiloxane, $Si_2O(NCO)_6$, melts at 44.5° into a colorless liquid boiling at 163° and 14 mm., or at 260° and 760 mm. with decomposition. It may be prepared from Si_2OCl_6 and silver isocyanate, or from silicon isocyanate and water, either with or without a solvent. Octoisocyanatotrisiloxane, $Si_3O_2(NCO)_8$, is a clear light-yellow liquid boiling at 170° and 2 mm.; it is made from $Si_3O_2Cl_8$ and silver isocyanate, rather than by controlled hydrolysis of silicon isocyanate. The existence of higher oxyisocyanates is indicated, but the separation of these would be exceptionally difficult.

2. Hexaisothiocyanatodisiloxane, $Si_2O(NCS)_6$, melting at 120–121°, is prepared from Si_2OCl_6 and silver isothiocyanate, followed by recrystallization from benzene.

3. Acetone and 1,4-dioxane are very good solvents for the oxyisocyanates, while benzene, carbon disulfide, carbon tetrachloride and diethyl ether are unexpectedly poor solvents, in view of the high solubility of silicon isocyanate in the same solvents.

CAMBRIDGE 38, MASS. RECEIVED JUNE 19, 1947

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(5) Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 452 (1876).

(6) Forbes and Anderson, *ibid.*, **66**, 1703 (1944).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Methyl Silicon Isothiocyanates. Molar Refractions

BY HERBERT H. ANDERSON

Previous efforts in this Laboratory to prepare certain complete series of mixed compounds have yielded monoisothiocyano derivatives[1] exclusively—silicon trimethoxyisothiocyanate and trichloroisothiocyanate; phosphorus difluoroisothiocyanate and dichloroisothiocyanate; phosphoryl dichloroisothiocyanate. Several considerations suggested that methyl groups in such molecules would greatly retard disproportionation and favor isolation of compounds containing two or three isothiocyano groups. The preparation of all three methyl silicon isothiocyanates has now fulfilled this prediction, and measurements of molar refractions have identified them as isothiocyanates.

Preparation of Methyl Silicon Isothiocyanates.—The Dow Corning Corporation of Midland, Michigan, kindly furnished the samples of pure trimethylchlorosilane, dimethyldichlorosilane and methyltrichlorosilane used in this investigation. In accordance with the established method,[2] a 30% excess of silver isothiocyanate converted each individual chloride into the corresponding isothiocyanate in benzene or hexane as a solvent; the yield was always about 85% of the theoretical amount. After thirty minutes at 80–90°, the suspended silver salts were filtered off and washed; the solution was then distilled. Repeated distillations in all-glass systems with a 50 cm., 4 mm. i.d. column without packing produced the follow-

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(1) Anderson, THIS JOURNAL, **67**, 223, 2176 (1945); **69**, 2495 (1947).

(2) Forbes and Anderson, *ibid.*, **62**, 761 (1940); Anderson, *ibid.*, **64**, 1757 (1942).

TABLE I

ANALYSES OF METHYL SILICON ISOTHIOCYANATES

Compound	% Isothiocyanate Found	% Isothiocyanate Calcd.	% Carbon Found	% Carbon Calcd.	% Hydrogen Found	% Hydrogen Calcd.	Mol. wt. Found	Mol. wt. Calcd
$(CH_3)_3Si(NCS)$	44.0	44.3	36.2	36.6	6.65	6.86	135 (Dumas)	131.2
$(CH_3)_2Si(NCS)_2$	66.2	66.7	27.4	27.6	3.40	3.44	183 (Dumas)	174.3
$(CH_3)Si(NCS)_3$	80.5	80.2	..	22.1	..	1.38	210 (Camphor)	217.3

TABLE II

PHYSICAL PROPERTIES OF SERIES, INCLUDING MOLAR REFRACTIONS

Compound	$(CH_3)_4Si$	$(CH_3)_3Si(NCS)$	$(CH_3)_2Si(NCS)_2$	$(CH_3)Si(NCS)_3$	$Si(NCS)_4$
B. p., °C.	26.5[5]	143.1 ± 0.3	217.3 ± 1.0	266.8 ± 1.0	313.0 314.2[6]
F. p. (m. p.), °C.	....	−32.8	18.0	72.4	143.8[6]
d^{20}_4, liquid	0.6480[5]	0.931	1.142	1.304[a]	ca. 1.409[a]
Index of refraction, 20°	1.3591[5]	1.4820 ± .0005	1.5677 ± .0005	....	....
Constants in vapor, A	....	7.7899	8.3006	8.4273	8.4484
Pressure equation, B	....	2043	2658	2995	3276
Calcd. heat of vaporization, cal./mole	....	9,350	12,150	13,700	13,900
Trouton constant	....	22.5	24.8	25.4	23.7
Soly. in organic solvents	high	high	high	limited[b]	limited[b]
Molar refraction, R, found, ml.	30.02[5]	40.18	49.92	59.8[a]	70.4[a]
R calcd. for isothiocyanates, ml.	(30.02)	40.05	50.07	60.09	70.12
	$(CH_3)_4Si$	$(CH_3)_3Si(SCN)$	$(CH_3)_2Si(SCN)_2$	$(CH_3)Si(SCN)_3$	$Si(SCN)_4$
R calcd. for thiocyanates, ml.	(30.02)	37.83	45.64	53.45	61.26

[a] Values obtained in solution by the law of mixtures. [b] The solid crystallized easily from benzene or carbon tetrachloride.

ing as middle fractions: trimethyl silicon isothiocyanate, $(CH_3)_3Si(NCS)$, b. p. 142.6–143.1° uncor., at 759 mm.; dimethyl silicon diisothiocyanate, $(CH_3)_2Si(NCS)_2$, b. p. 99.0–99.5° at 14 mm.; also, methyl silicon triisothiocyanate, $(CH_3)Si(NCS)_3$, b. p. 145–146° at 15 mm.

Analyses, including Molecular Weights; see Table I.—Isothiocyanate was determined through decomposition of each individual compound by absolute ethanol, addition of water after two minutes, and titration with silver nitrate solution in the presence of ferric nitrate as indicator. The molecular weight of $CH_3Si(NCS)_3$ obtained by the depression of the freezing point of camphor is somewhat low because of slight hydrolysis by atmospheric moisture. A solution of potassium dichromate in concentrated sulfuric acid absorbed nitrogen dioxide completely[3]—a great improvement over the older lead dioxide method—and thus made possible sufficiently accurate determinations of carbon and hydrogen by combustion.

Physical Properties; see Table II.—Dynamic vapor pressure measurements, made upon the day of final purification and using calibrated mercury thermometers, served for calculations of heats of vaporization and Trouton constants. The three equations fitted seventeen out of eighteen observed pressures with an over-all average error of 2 mm. and a maximum error of 6 mm. Values on $Si(NCS)_4$ were also obtained, but these were good only to 6 mm. on the average. Viscous liquids and glasses did not appear during determinations of freezing points. The densities and indices of refraction of the two liquids were observed at 20°. To obtain the molar refractions of $(CH_3)Si(NCS)_3$ and $Si(NCS)_4$, sufficient dimethyl silicon diisocyanate, $(CH_3)_2Si(NCO)_2$, was added to dissolve the former while methyl silicon triisocyanate, $(CH_3)Si(NCO)_3$, was added to the latter; the law of mixtures was applied. Information on these new methyl silicon isocyanates will be submitted for separate publication elsewhere in THIS JOURNAL.

The hydrolysis of liquid methyl silicon isothiocyanates was moderately slow—fortunate since the analyses were made without elaborate protection from atmospheric moisture. Dimethyl silicon diisothiocyanate, upon complete hydrolysis, yielded a liquid product which floated on water, and which after drying showed an average b. p. of 260°; cyclic dimethyl siloxanes[4] were presumably the main constituents present.

Assumptions and Comparisons

A brief correlation of certain molar refractions (n^2 formula) is presented at this point. Values in ml. taken as standard include: Cl, 5.97; C, 2.42; O, 1.64; H, 1.10. After examining calculations based on nineteen compounds, chiefly organic, the author has evaluated R_{SCN} as 13.53 ± 0.02 ml., and R_{NCS} as 15.83 ± 0.10 ml. in non-conjugated

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(3) Elving and McElroy, *Ind. Eng. Chem., Anal. Ed.*, **13**, 660 (1941)

(4) Hunter, Hyde, Warrick and Fletcher, THIS JOURNAL, **68**, 667 (1946).

(5) Bygden, *Z. physik. Chem.*, **90**, 243 (1915).

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

systems. If one assumes constancy for carbon, hydrogen, oxygen, chlorine and isothiocyanate, R_{Si} has the following values: in $SiCl_4$, 4.84; in $Si(CH_3)_4$, 7.14; in $Si(OCH_3)_4$, 3.88; in $Si(NCS)_4$, 6.80 ml. R_{Si} was estimated for isothiocyanates through linear interpolation between the values for the binary compounds; for example, the value for $(CH_3)_2Si(NCS)_2$ was 6.97 ml., half-way between 7.14 and 6.80 ml. To predict the molar refractions of methyl silicon *thiocyanates*, R_{Si} was taken as a constant, 7.14 ml., as in $Si(CH_3)_4$. Table II shows that the experimental molar refractions of the methyl silicon isothiocyanates agree closely with values calculated for isothiocyanates.

A previous paper[1] stated, "This issue of structure is still unsettled, and may presently be decided by examination of molar refractions of the thiocyanate group; preliminary calculations have been made, but these rest upon two compounds only." The structure of "$Si(OCH_3)_3SCN$" mentioned in the same paper[1] and that of "$SiCl_3(SCN)$" previously[1] isolated may now be identified as *isothiocyanate.* The observed molar refractions of 41.86 and 39.19 ml. (density adjusted from 24 to 20°) agree with values of 42.52 and 39.07 ml., respectively, calculated for isothiocyanates—in contrast with 40.22 and 36.77 ml. expected for thiocyanates.

Like the methylchlorosilanes, the methyl silicon isothiocyanates do not follow Swarts' rule[7] of linear increase in boiling points. Boiling points calculated by the "increment method," adding 64.1° to the b. p. of the corresponding chloride for each successive replacement of one chloride[2] by *isothiocyanate*, are also too low. Table III presents this comparison.

TABLE III

BOILING POINTS, °C.

Compound	Calcd. by Swarts' method	Calcd. by "increment method"	Actua
$(CH_3)_3Si(NCS)$	98	121.8 (57.7 + 64.1)	143.1
$(CH_3)_2Si(NCS)_2$	170	198.2 (70.0 + 128.2)	217.3
$(CH_3)Si(NCS)_3$	242	258.0 (65.7 + 192.3)	266.8

Like other methyl silicon halides, the vapor of $(CH_3)_3Si(NCS)$ has a disagreeable odor and a possible toxicity.

The author thanks Professor George S. Forbes of this Laboratory for helpful suggestions.

Summary

1. Each of the three methylchlorosilanes reacts with silver isothiocyanate to produce a (new) methyl silicon isothiocyanate. Trimethyl silicon isothiocyanate, $(CH_3)_3Si(NCS)$, melts at −33° and boils at 143°; dimethyl silicon diisothiocyanate, $(CH_3)_2Si(NCS)_2$, melts at 18° and boils at 217°; methyl silicon triisothiocyanate, $(CH_3)Si(NCS)_3$, melts at 72° and boils at 267°. These are the only known silicon compounds containing two or three isothiocyanate groups.

2. Densities, indices of refraction and vapor pressure equations are given. The observed molar refractions in ml.—$(CH_3)_3Si(NCS)$, 40.2; $(CH_3)_2Si(NCS)_2$, 49.9; $(CH_3)Si(NCS)_3$, 59.8; $Si(NCS)_4$, 70.4—agree closely with values calculated for the isothiocyanates.

CAMBRIDGE, MASS. RECEIVED JULY 9, 1947

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(7) Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Manganous Ion–Manganese Dioxide Electrode

BY A. WITT HUTCHISON

The July, 1930, issue of "The Journal of the American Chemical Society" contained two papers dealing with the manganous ion–manganese dioxide electrode. Brown and Liebhafsky[1] in the first of these describe measurements made on the cell $H_2/HClO_4$ (m_1), $Mn(ClO_4)_2$ (m_2)/MnO_2(s) at 25° with varying molalities of acid and manganous perchlorate. From the results of their measurements the authors reported for the molal potential of the electrode reaction

$$MnO_2(s) + 4H^+ + 2e = Mn^{++} + 2H_2O \qquad (1)$$

a value of +1.236 v. which they stated "is probably correct within 2 mv."

In the second paper Popoff, Riddick and Becker[2] discuss their unsuccessful attempts to obtain consistent and reproducible values for the potentials of the same cells when highly purified manganese dioxide was used. They concluded that the difference between the two studies lay in the manner of preparation and purity of the manganese dioxide and that the cell was irreversible when pure manganese dioxide was employed. These authors stated that "...serious polarization may be expected to take place at electrodes which involve reactions that take place with a change in the oxygen content..." and referred to Lewis and Randall[3] for support for this generalization. The section referred to actually deals with possible polarization of an electrode process consisting of a change in the oxygen content of an

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(1) Brown and Liebhafsky, THIS JOURNAL, **52**, 2595 (1930).

(2) Popoff, Riddick and Becker, *ibid.*, **52**, 2624 (1930).

(3) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 388.