[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Chloro(iso)cyanates of Silicon, Including Rearrangements at High Temperatures

BY HERBERT H. ANDERSON

Numerous series of volatile mixed halides have been discovered in the past, such as fluorochlorides, fluorobromides, fluorochlorobromides, chlorobromides, chloroiodides and bromoiodides. Their physical properties have been investigated moderately well, but comparatively little is known of their stabilities under various conditions. Recent work in this Laboratory has established the existence of volatile (iso)cyanates, and of one volatile cyanate: $Si(NCO)_4$,[1] $Ge(NCO)_4$,[2] $P(NCO)_3$,[1] $PO(NCO)_3$,[3] $PS(NCO)_3$,[2] and $As(NCO)_3$[3]; also $Si(OCN)_4$.[1] Thiocyanates are known also: $Si(SCN)_4$,[4] $P(SCN)_3$,[5] and $PO(SCN)_3$.[3] *This report* includes the isolation of all three chloro(iso)cyanates of silicon, and a study of their thermal rearrangements. *Further work*, now nearing completion, concerns chloro(iso)cyanates of phosphorus and phosphorus, chlorothiocyanates of silicon and phosphorus, and chlorobromides of carbon, silicon and germanium.

Preparation of Silicon Chloro(iso)cyanates.—Methods are listed in the order of importance.

(a) **Interaction of Silicon Tetrachloride and Silicon (iso)cyanate at 600°.**—A mixture of 66 ml. of $SiCl_4$ and 70 ml. of $Si(NCO)_4$[1] was passed slowly through a hot tube. A separatory funnel with constricted outlet served in regulating the drip of the liquid over a two-hour period. The first distillation yielded crude fractions of 10 ml. of $SiCl_4$, 32 ml. of $SiCl_3(NCO)$, 45 ml. of $SiCl_2(NCO)_2$, 35 ml. of $SiCl(NCO)_3$, and 11 ml. of $Si(NCO)_4$. Boiling points were 86.8° for $SiCl_3(NCO)$, 117.8° for $SiCl_2(NCO)_2$, and 152° for $SiCl(NCO)_3$. The redistillation of each of the above fractions was limited to a two-hour period to minimize decomposition; the boiling point ranges of fractions collected for measurements did not exceed 0.5°.

(b) **Sealed Tube Method; $SiCl_4$ and $Si(NCO)_4$.**—Fifteen ml. of $Si(NCO)_4$ and 11.3 ml. of $SiCl_4$ were heated in a Carius tube for seventy hours at 135°. Products were 4.8 ml. of $SiCl_4$, 2.8 ml. of $SiCl_3(NCO)$, 3.3 ml. of $SiCl_2(NCO)_2$, 6.5 ml. of $SiCl(NCO)_3$, and 6.0 ml. of $Si(NCO)_4$. On the basis of equilibria shown later in Table II, a period of a week at 135° would be required for random rearrangement of the products.

(c) **Gradual Addition of AgNCO to a Large Excess of $SiCl_4$ in Solution.**—The possibility of making chloro(iso)cyanates by very gradual addition of silver (iso)cyanate was considered. A mixture of 90 ml. of $SiCl_4$, 35 ml. of CS_2, and 70 ml. of C_2H_5Br was used; 80 g. of silver (iso)cyanate was added in small portions, over a period of an hour, with constant and vigorous shaking. The liquid boiled slowly because of the heat of reaction. Distillation yielded 6.8 ml. of $SiCl_3(NCO)$, 5.5 ml. of $SiCl_2(NCO)_2$, and 5.7 ml. of $Si(NCO)_4$; $SiCl(NCO)_3$ was absent, or less than 0.3 ml. This method is important, although not so valuable as the high temperature method, which gives all three compounds.

Chloro(iso)cyanates as by-products in the preparation of $Si(NCO)_4$, as previously described[1]: 517 g. of AgNCO and 108 ml. (9 ml. excess) of $SiCl_4$ were used. Redistillation of the fraction boiling between 95 and 183° yielded 0.8 g. of $SiCl_2(NCO)_2$, 3.3 g. of $SiCl(NCO)_3$, 147 g. of $Si(NCO)_4$ and an estimated 5 g. of $Si(OCN)_4$. On a basis of (iso)-cyanate, the yield exceeded 90%. It has been found advisable to use about this excess of silicon tetrachloride, in order to convert the silver (iso)cyanate completely into silver chloride.

Analysis.—A weighed sample was frozen and dropped beneath a 6-cm. column of absolute alcohol in a test-tube; ethyl silicate, ethyl cyanate (or isocyanate), and hydrogen chloride were the products. Water was added immediately. This method is superior to decomposition by water with the consequent formation of silica gel. Chloride was determined with standard silver nitrate solution, using potassium chromate as indicator. For $SiCl_3(NCO)$: calcd. 60.28% Cl; found 60.1, 60.5. For $SiCl_2(NCO)_2$ calcd. 38.75% Cl; found 38.6, 38.9. For $SiCl(NCO)_3$ calcd. 18.70% Cl; found 18.8, 18.9. Molecular weights were found by the Dumas method. For $SiCl_3(NCO)$ calcd. 176.45; found 176, 180. For $SiCl_2(NCO)_2$ calcd. 183.01; found 180, 188. For $SiCl(NCO)_3$ calcd. 189.57; found 193, 196.

Physical Properties.—All three chloro(iso)cyanates are colorless liquids characterized by a peculiar "isocyanate odor." Boiling points were measured to 0.5°, immediately followed by measurement of the boiling point of pure benzene or water or bromobenzene under identical conditions. Densities were measured at 25°, using a 1.7 ml. bulb with a long capillary inlet bearing a reference mark. The height of the meniscus was measured in each case.

The system was calibrated with water and probably gave densities good to two parts per thousand. The index of refraction was measured with an Abbe refractometer (calibrated with water and carbon tetrachloride) in white light at 20°.

Melting points were determined using about 3 ml. of pure sample and a toluene thermometer, with its bulb wholly immersed in the liquid. This thermometer was calibrated at 0 and −78°; melting point ranges were much less than a degree. Table I shows the trends in properties from $SiCl_4$ through to $Si(NCO)_4$.[1] The calculation of boiling points of $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$ by linear interpolation between those of $SiCl_4$ and $Si(NCO)_4$ gave 89.6°, 121.6°, and 153.6°. The average observed value falls 2.6° lower than the calculated figure—a reasonable agreement.

TABLE I

Compound	B. p., °C.	M. p., °C.	Density, 25°	n	Molecular vol., ml.
$SiCl_4$	57.57	−70	1.469[6]	1.4126	115.7
$SiCl_3(NCO)$	86.8	−69 ±1.5	1.445	1.4262	122.4
$SiCl_2(NCO)_2$	117.8	−80 ±1.5	1.437	1.4380	127.3
$SiCl(NCO)_3$	152.0	−35 ±1.5	1.437	1.4507	131.9
$Si(NCO)_4$[1]	185.6	26.0	1.434[a]	1.4610	136.8

[a] Pycnometric value recently obtained.

Boiling points and indices of refraction are the best means of physical identification of members of the series. Melting points and densities are less distinctive.

Chemical Properties.—All three chloro(iso)cyanates of silicon, like other (iso)cyanates, are vigorously decomposed by water, with the formation of gas bubbles; they react vigorously with alcohol, but no bubbles appear. The (NCO) group in this series is quite stable at 600°. Oxidation is negligible in air at 200°.

Rearrangements of Chloro(iso)cyanates of Silicon.—As shown in the section on preparation, $SiCl_4$ and $Si(NCO)_4$

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[1] Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

[2] Forbes and Anderson, *ibid.*, **65**, 2271 (1943).

[3] Anderson, *ibid.*, **64**, 1757 (1942).

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

[5] Miquel, *Ann. Chim. Phys.*, [V] 11, 343 (1877); Dixon, *J. Chem. Soc.*, **79**, 541 (1901).

[6] See Mellor, "Comprehensive Treatise," Vol. VI, p. 962. Density at 20° is 1.483.

TABLE II

REARRANGEMENTS OF SILICON CHLORO(ISO)CYANATES

Run	Initial Mixture	Atom % Cl Initial	Atom % Cl Final	$SiCl_4$	$SiCl_3(NCO)$	$SiCl_2(NCO)_2$	$SiCl(NCO)_3$	$Si(NCO)_4$
1	$^1/_2$ $SiCl_4$ + $^1/_2$ $Si(NCO)_4$	0.50	0.50	found 8	25	34	25.0	8.0
				calcd. 6.25	25.0	37.5	25.0	6.25
2	pure $SiCl_2(NCO)_2$	.50	.50	found 8	25	34	26	7
				calcd. 6.25	25.0	37.5	25.0	6.25
3	pure $SiCl_3(NCO)$	.75	.75	found 33	38	24	5	(0)
				calcd. 31.6	42.2	21.1	4.7	0.4
4	pure $SiCl(NCO)_3$	.25	.26	found (0)[a]	5.0	26	36	33
				calcd. 0.4	4.7	21.1	42.2	31.6

[a] Too small for satisfactory measurement, although $SiCl_3(NCO)$ started to distill at 80°, instead of 87°.

react together; all five possible compounds are produced in amounts predictable by assuming random distribution of groups. Previous work on redistribution in the lead alkyl series[7] indicated random distribution of groups, and included a method of calculating the percentage occurrence of each compound. Thermal rearrangement of individual compounds ($SiCl_3(NCO)$, $SiCl_3(NCO)$, and $SiCl(NCO)_3$) was studied carefully; vapor was passed through a hot tube at 600°, at a slow rate, with later determination of products by fractional distillation. Table II summarizes the results.

Experimental Work on Rearrangements.—The redistribution between $SiCl_4$ and $Si(NCO)_4$ was done on a large scale and produced large amounts of the compounds desired, as explained at the beginning of the section on preparation. By adjusting the amounts found according to molecular volumes (Table I), the correct molecular ratios were obtained. Rearrangements of $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$ were obtained by the passage of 5 ml. of each pure compound through a small Pyrex tube at 600°, over a period of thirty minutes. Values in Table II have been rounded off to the nearest per cent. More precise and therefore slower distillation would have led to secondary rearrangements of considerable magnitude. Amounts of less than 2% are difficult to determine, notably if the least volatile compound is involved. Volumes were measured to 0.05 ml. in calibrated receivers of the same bore and with nearly flat bottoms.

The percentages indicate random distribution within a few per cent. Secondary rearrangements are too close for attainment of theoretical ratios. Values of the chief component are a little low in all cases, but this is within experimental error, and without significance.

A sample of $SiCl_2(NCO)_2$ rearranged to the extent of several per cent. after standing four months at room temperature. Mixtures of $Si(NCO)_4$ and $SiCl_4$, as well as the three chloro(iso)cyanates, are being set aside at room temperature with the intention of determining the distribution of products after considerable time intervals.

The author is much indebted to Professor George S. Forbes of this Laboratory for many helpful suggestions. Other work on rearrangement of mixed halides and on cyanates and thiocyanates is in progress and will be reported soon.

Summary

1. $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, and $SiCl(NCO)_3$ have been prepared. The progression of several physical properties in the series $SiCl_4$ through $Si(NCO)_4$ has been tabulated. $SiCl_4$ and $Si(NCO)_4$ react rapidly at 600° to give all three chloro(iso)cyanates. Interaction is moderate in rate at 135°, and extremely slow at room temperature. Gradual addition of AgNCO to a large excess of $SiCl_4$ in solution yields $SiCl_3(NCO)$ and $SiCl_2(NCO)_2$, but no $SiCl(NCO)_3$.

2. Random distribution, such as previously found by Calingaert, Beatty and Soroos in the lead alkyl series, also applies to the rearrangement of any mixture or pure compound in the series $SiCl_4$ through $Si(NCO)_4$. No catalyst is needed.

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[7] Calingaert, Beatty and Soroos, THIS JOURNAL, 62, 1100 (1940).

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A Study of Organic Parachors. VI. A Supplementary Series of Tertiary Alcohols[1]

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The parachor values for a series of tertiary alcohols[2] have been previously reported from this Laboratory and values for the CH_2 group in various positions have been determined and suggested as a means of calculating the parachors of other tertiary alcohols. Nine additional supplementary tertiary alcohols have been prepared and their refractive indices, densities, surface tensions and parachors have been determined. The alcohols were prepared by standard methods and were purified by successive vacuum distillations.[3] To minimize decomposition the temperatures of distillation were kept below 75°. Refractive indices were determined at 20, 25 and 35°. Densities and surface tensions were measured at 25, 45 and 55°, and the parachors were calculated for the same temperatures, using the standard formula $P = M\gamma^{1/4}/(D - d)$. The data obtained are shown in Table I. The varia-

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[1] The authors wish to express their gratitude to Professor E. Emmet Reid, Research Consultant to the department, for his continued interest and suggestions in connection with this investigation.

[2] K. Owen, O. R. Quayle and E. M. Beavers, THIS JOURNAL, 61, 900 (1939).

[3] Prepared by Harry M. Stubbs of this Laboratory.