The selected portion includes all compositions at which molecular compound formation might reasonably be expected to occur. The melting point data for this system are listed in Table VI and are diagrammed in Fig. 5.

An examination of the diagram shows a considerable degree of similarity with the silicon tetrabromide and cyclohexane systems with dioxane. No stable compound is indicated and the same type of curvature change occurs in the liquidus at about the same temperature.

Previous determinations[2] of the electric moment of silicon tetrachloride in dioxane gave zero value. If the small moment obtained for silicon tetrabromide in dioxane is attributed to an electronic interaction between the halogens and the donor oxygens of dioxane, the zero value of the moment for silicon tetrachloride in dioxane would indicate a lessened tendency for such interaction. Attempts to obtain reproducible warming curves for silicon tetrachloride–dioxane solutions in the neighborhood of 80 mole % dioxane were unsuccessful.

Summary

1. Melting point–composition diagrams for the systems of silicon tetrabromide, silicon tetrachloride and cyclohexane with dioxane have been determined.

2. A metastable form of solid silicon tetrabromide, m. p. 2.3°, has been observed.

3. Thermal analysis of the system silicon tetrabromide–dioxane indicates the existence of an unstable 1:4 complex.

4. A characteristic curvature change in the liquidus for several systems containing dioxane was found to occur at approximately 0°.

5. Dielectric constant and density data indicate a small degree of electronic interaction between silicon tetrabromide and dioxane. The electric moment of silicon tetrabromide in carbon tetrachloride was found to be 0.0.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phenyl and Ethoxy Silicon Isocyanates

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

This paper describes two complete series of new mixed silicon isocyanates. The phenyl silicon isocyanates were prepared from phenylchlorosilanes and silver isocyanate, and the three ethoxy silicon isocyanates from ethoxychlorosilanes and silver isocyanate.

Preparation of Phenyl Silicon Isocyanates.—In the usual manner,[1] each phenylchlorosilane was changed into the corresponding isocyanate through reaction with an excess of silver isocyanate; the yields varied from 75 to 90%. All three phenyl silicon isocyanates were distilled at 3 mm. pressure through a plain column 4 mm. i. d. and 300 mm. long. Triisocyanate, collected from 101 to 102°; diisocyanate, 142–143°; monoisocyanate, 177.5–178.5°.

Physical Properties and Analyses of Phenyl Silicon Isocyanates (see Table I).—Dynamic vapor pressure measurements were made on each of the three compounds—six values on the triisocyanate, five on the diisocyanate and four on the monoisocyanate. Frozen phenyl silicon triisocyanate melted over the range −50 to −20°, approximately. Possibly two solid forms were present; diphenyl silicon diisocyanate supercooled to −70°, but formed a crystalline solid of sharp m. p. after addition of a small clay chip to promote crystallization; triphenyl silicon isocyanate supercooled less than 20°. Needless to say, vigorous stirring was essential in obtaining melting points. When shaken with water, the triisocyanate hydrolyzed slowly at first and then with increasing speed; the diisocyanate hydrolyzed at a moderate rate only, even with vigorous shaking; the monoisocyanate, however, hydrolyzed very slowly, if at all. Analyses employed the Dumas method for nitrogen, combustion for carbon and hydrogen, and the hydrolysis and ignition of the triisocyanate to obtain silica as the end-product. Calcd. for $(C_6H_5)Si(NCO)_3$: Si, 12.2; C, 46.8; H, 2.2. Found: Si, 12.3; C, 47.1; H, 2.3. Calcd. for $(C_6H_5)_2Si(NCO)_2$: N, 10.5; H, 3.8. Found: N, 10.8; H, 3.5. Calcd. for $(C_6H_5)_3Si(NCO)$: N, 4.6; H, 5.0. Found: N, 4.4; H, 5.3 The observed molecular weights in camphor solution were 212, 250 and 290, respectively, corresponding to the calculated values 231, 266 and 301.

Preparation of Ethoxy Silicon Isocyanates.—Methanol reacts with silicon isocyanate to produce methoxy silicon isocyanates,[2] the boiling points of which are 15° apart; however, the reaction between ethanol and silicon isocyanate yields products difficultly separable. It was much easier to obtain the desired products from the ethoxychlorosilanes. Ethoxytrichlorosilane, prepared from tetrachlorosilane and ethanol, boiled at 102.1° at 758 mm.[3]; diethoxydichlorosilane boiled at 137.4–137.6° at 754 mm.[3] Triethoxychlorosilane boiled from 154 to 157°,[4] even upon repeated distillation on a plain column 4 mm. i. d., 125 cm. long; apparently redistribution limited the purity of the sample. Following the general method,[1] a solution of the individual ethoxychlorosilane in benzene was heated with a 30% excess of silver isocyanate for thirty minutes at 90°, and then filtered with washing of the silver salts; benzene was removed by distillation at atmospheric pressure. The middle fraction of ethoxy silicon triisocyanate boiled at 178.5° uncor. at 764 mm. with little variation; that of diethoxy silicon diisocyanate boiled at 174.8–174.9° uncor. at 760 mm. in a column without spiral or packing, and 4 mm. i. d. and 50 cm. long.

Triethoxy silicon isocyanate could not be purified by distillation alone; the main contaminant was probably diethoxy silicon diisocyanate, the boiling point of which is only 2.5° higher, and the minor contaminant was the more easily removed ethyl orthosilicate (tetraethoxysilane). The first preparation showed a b. p. of 173.5°, d^{20}_4 1.025 and n (index of refraction) 1.3933, leading to R (molar refraction, n^2 formula) 47.82 ml., none of which agreed with values interpolated in the series. A product of apparently higher purity was next obtained by treatment of the above material with ethanol in excess. Prob-

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

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

(3) Peppard, Brown and Johnson, *ibid.*, **68**, 70 (1946), reported 101.5–102.0°, 136.0–136.5° and 156.0–156.5°, respectively, at 760 mm.

TABLE I

PHENYL SILICON ISOCYANATES

Compound	$Si(NCO)_4$[1]	$(C_6H_5)Si(NCO)_3$	$(C_6H_5)_2Si(NCO)_2$	$(C_6H_5)_3Si(NCO)$	$Si(C_6H_5)_4$
B. p., °C.	185.6	251.9 ± 1°	319.6 ± 1°	372.0 ± 1°	428[b]
M. p., °C.	26	Indefinite	22.9 ± 0.3°	95.0 ± 1°	233[b]
d^{20}_4	1.442[a]	1.273	1.188	....	..
Index of refraction, 20°, ±0.0010	1.4610	1.5210	1.5675	....	..
Molar refraction, ml. Found	37.29	55.45	73.3	....	..
Molar refraction, ml. Calcd.	......	55.40	73.5		
Constants in vapor pressure equation A	9.0198	8.6663	8.6683	8.3234	..
Constants in vapor pressure equation $-B$	2816	3038	3421	3511	..
Heat of vaporization, calcd., kcal.	12.9	13.9	15.7	16.1	..
Trouton constant	26.5	26.4	26.5	24.9	..

[a] Calculated from density at 25°. [b] Lewis and Newkirk, THIS JOURNAL, **69**, 701 (1947).

TABLE II

PROPERTIES OF ETHOXY SILICON ISOCYANATES

Compound	$(C_2H_5O)_4Si$	$(C_2H_5O)Si(NCO)$	$(C_2H_5O)_2Si(NCO)_2$	$(C_2H_5O)Si(NCO)_3$	$Si(NCO)_4$
B. p., °C.	165.5[a]	172.9 ± 0.5	175.4 ± 0.5	179.6 ± 0.5	185.6 ± 0.5
Index of refraction at 20° ±0.0005	1.3862[b]	1.3922	1.4046	1.4251	1.4610
d^{20}_4	0.933[a]	1.015 ± 0.004	1.108	1.236	1.442[c]
Molar refraction, ml. Found	52.05[d]	48.2	44.71	41.06	37.29
Molar refraction, ml. Calcd.	...	48.36	44.67	40.98	....
Vapor pressure constants A	...	8.2179	8.2577	8.4374	9.0198
Vapor pressure constants $-B$	...	2380	2411	2515	2816
Heat of vaporization, calcd., kcal.	...	10.9	11.0	11.5	12.9
Trouton constant	...	24.4	24.6	25.4	26.5

[a] Average of acceptable published data. [b] Solana and Moles, *C. A.*, **27**, 1252 (1933). [c] Estimated from d^{25}_4 1. 434. [d] Bygden, *Z. physik. Chem.*, **90**, 243 (1915).

ably the diethoxy impurity was thus converted into the desired triethoxy compound. As shown below, the diisocyanate is destroyed by alcohol or water more rapidly than is the monohalide. Eighteen milliliters of absolute ethanol was added to 90 g. of triethoxysilicon isocyanate, over a period of forty minutes, and then unchanged ethanol was removed by distillation; after further purification, the triethoxy derivative was found to have the analyses given below and the following physical properties: b. p. 172.9°, d^{20}_4 1.015, n 1.3922, R, 48.19 ml. A second similar treatment with ethanol produced a sample of b. p. 172.8°, d^{20}_4 1.009, n 1.3917 and R 48.41. A third treatment with ethanol followed by shaking with a moderate amount of 0.06 M sodium hydroxide, drying and repurification resulted in a product of b. p. 173.2°, d^{20}_4 1.003, n 1.3902 and R 48.51 ml. When values of d^{20}_4 and of n were graphed for the series from silicon tetraisocyanate to tetraethoxysilane exclusive of the triethoxy compound, the curves were quite smooth and predicted the following values: d^{20}_4 1.013 ± 0.005, n 1.3921 ± 0.0003. Corresponding data, as yet unpublished, for the methyl silicon isocyanates, and for the methyl silicon isothiocyanates, also lie on smooth curves. It was concluded that the product of boiling point 172.9°, obtained through a single treatment with ethanol, was the purest of the four.

Analyses of Ethoxy Compounds.—Carbon and hydrogen were obtained by combustion, and the Dumas method was used for nitrogen. Calcd. for $(C_2H_5O)_3Si(NCO)$: C, 41.0; H, 7.3; N, 6.8. Found: C, 40.8; H, 7.4; N, 6.7. Calcd. for $(C_2H_5O)_2Si(NCO)_2$: C, 35.6; H, 5.0; N, 13.9. Found: C, 36.0; H, 4.9; N, 13.6. Calcd. for $(C_2H_5O)Si(NCO)_3$: C, 30.1; H, 2.5; N, 21.1. Found C, 29.8; H, 2.6; N, 21.2. The molecular weights observed by the Dumas method were 208, 206 and 205 respectively, corresponding to calculated values of 205, 202 and 199.

Physical Properties of Ethoxy Silicon Isocyanates (See Table II).—Dynamic vapor pressure measurements, made on the day of final purification and using calibrated thermometers, served for calculations of heats of vaporization. The vapor pressure equations fit eighteen observed points with an average deviation of three mm. Swarts' rule of linear progression[4] of boiling points predicts 170.5, 175.5 and 180.6° for the new isocyanates, in reasonable agreement with observed values. All were colorless liquids. Densities were taken using a special 2-ml. micropycnometer. Rates of hydrolysis decreased strikingly from silicon isocyanate to tetraethoxysilane.

Summary

Each of the three phenylchlorosilanes and also each of the three ethoxychlorosilanes yielded the corresponding new isocyanate upon treatment with silver isocyanate. Triphenylsilicon isocyanate, $(C_6H_5)_3Si(NCO)$, boiled at 372°; diphenylsilicon diisocyanate, $(C_6H_5)_2Si(NCO)_2$, at 320°; phenylsilicon triisocyanate, $(C_6H_5)Si(NCO)_3$, at 252°; triethoxysilicon isocyanate, $(C_2H_5O)_3Si(NCO)$, at 172.9°; diethoxysilicon diisocyanate, $(C_2H_5O)_2Si(NCO)_2$, at 175.4°; ethoxysilicon triisocyanate, $(C_2H_5O)Si(NCO)_3$, at 179.6°.

Densities, refractive indices, molar refractions and vapor pressure equations were determined.

Substitution of phenyl or of ethoxy groups progressively decreases rates of hydrolysis of the isocyanate groups present.

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[4] Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).