bility is not a linear function of the number of chlorine atoms present, and therefore a strictly additive rule will not apply. The carbon tetrafluoride–carbon tetrachloride and trifluoromethane–chloroform series give curves which are nearly linear. The slopes, however, are different. If a chlorine atom in carbon tetrachloride or fluorotrichloromethane is replaced by fluorine, the susceptibility drops about 7.3 units; whereas in chloroform and fluorodichloromethane the drop is 10.1 units. According to Pascal's constants, the susceptibility should decrease by 8.6 units. Unfortunately, we were unable to measure the susceptibilities of carbon tetrafluoride, fluorotrichloromethane, and trifluoromethane in our apparatus since their vapor pressures at room temperature are quite high. If one extrapolates the curves as straight lines, one obtains -36.8×10^{-6}, -44.2×10^{-6} and -28.3×10^{-6} as the molar susceptibilities for these compounds, respectively.

The data on the ethylenic derivatives are illustrated in Fig. 3. The molar susceptibilities are practically a linear function of the number of chlorine atoms present in the molecule. However, *trans*-chloroethylene and vinylidene chloride have measurably lower susceptibilities than the *cis*-isomer. The decrease in susceptibility which results when a chlorine atom is replaced by fluorine in a chloro–fluoro ethylene is 11.0 units. In the ethylene–perchloroethylene series the decrease is 15.3 units when chlorine is replaced by hydrogen. Pascal's constants give 17.2 for the latter. A linear extrapolation of the curves in Fig. 3 gives -38.2×10^{-6} and -20.6×10^{-6} for the molar susceptibilities for tetrafluoroethylene and ethylene, respectively. The latter figure agrees well with -18.22×10^{-6} which can be calculated from Pascal's constants but deviates widely from the values of -44.8×10^{-6} given in the "International Critical Tables."[11]

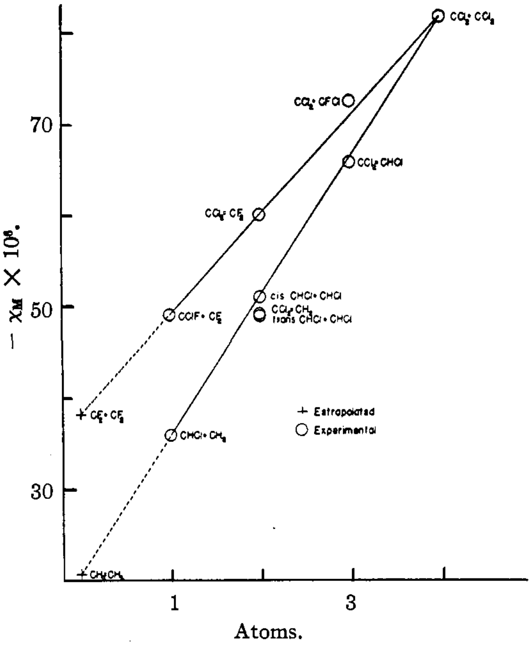

Fig. 3.—Diamagnetic susceptibilities of some fluoro and chloro derivatives of ethylene.

Acknowledgment.—We wish to thank Mr. P. W. Trott for preparing samples of $CCl_2{=}CH_2$ and $CCl_2{=}CFCl$. Dr. M. L. Sharrah carried out the measurements on the *cis*- and *trans*-dichloroethylenes.

Summary

An apparatus is described for measuring the susceptibilities of liquids under pressure. Diamagnetic susceptibilities of the following compounds were determined: CCl_3F, CCl_2F_2, $CHCl_2F$, $CHClF_2$, $CCl_2{=}CCl_2$, $CCl_2{=}CHCl$, $CCl_2{=}CH_2$, $CHCl{=}CHCl$ *cis* and *trans*, $CHCl{=}CH_2$, $CCl_2{=}CClF$, $CCl_2{=}CF_2$, and $CClF{=}CF_2$. The data give, by extrapolation, an estimate of the susceptibilities of the following compounds: $CClF_3$, CF_4, CHF_3, C_2H_4, and C_2F_4. The relationship of the data obtained to Pascal's constants is discussed. It was found that *trans*-dichloroethylene and vinylidene chloride have measurably lower susceptibilities than the corresponding *cis*-isomer.

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[CONTRIBUTION FROM WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Ethylgermanium Isocyanates

BY HERBERT H. ANDERSON

Six binary volatile inorganic isocyanates resulted from previous investigations: silicon tetraisocyanate,[1] believed to be the first volatile inorganic isocyanate ever prepared; phosphorus triisocyanate[1]; thiophosphoryl triisocyanate[2]; phosphoryl triisocyanate[3]; arsenic triisocyanate[3]; germanium tetraisocyanate, isolated both by the author (in June, 1942),[2] and by Laubengayer and Reggel[4] at Cornell University.

However, not all ternary derivatives containing isocyanate were capable of isolation. Germanium chloroisocyanates[5]—as well as germanium chlorobromides[6]—could not be purified by distillation, whereas methylsilicon isocyanates,[7] silicon chloroisocyanates,[8] phosphorus fluoroisocyanates[9] and numerous other such compounds could be distilled.

This paper in turn reports all three possible ethylgermanium isocyanates.

Preparation of Ethylgermanium Isocyanates.—Professor Eugene G. Rochow, of Harvard University, kindly furnished pure samples of ethyltrichlorogermane and diethyldichlorogermane, boiling at 140.0 and 172.8°, respectively, under 763 mm. pressure. Germanium tetrachloride, prepared and previously studied by the present author at Harvard University[2,5,6] was made available as a starting material.

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(1) to (3) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940); **65**, 2271 (1943); Anderson, *ibid.*, **64**, 1757 (1942).

(4) Laubengayer and Reggel, *ibid.*, **65**, 1783 (1943).

(5), (6) Forbes and Anderson, *ibid.*, **67**, 1911, 1703 (1945); **66**, 931 (1944).

(7) to (9) Forbes and Anderson, *ibid.*, **70**, 1222 (1948); Anderson, *ibid.*, **66**, 934 (1944); **69**, 2495 (1947). Also other publications by the same authors.

TABLE I

PROPERTIES OF ETHYLGERMANIUM ISOCYANATES

Compound	B. p., °C.	M. p., °C.	d^{20}_4	n^{20}_D ±0.0010	R, ml.	A and B in $\log P = A - B/T$	Calcd. ΔH, kcal.	$\Delta H/T_B$
$(C_2H_5)_4Ge$	164.7 ± 0.5[11]	−90[12]	0.9932[13]	1.4430	50.41	7.6938 2107	9.6	22.0
$(C_2H_5)_3Ge(NCO)$	200.4 ± 0.5	−26.4 ± 1.0	1.1514	1.4519	47.25[14]	7.9424 2396	11.0	23.1
$(C_2H_5)_2Ge(NCO)_2$	226.0 ± 0.5	−32 ± 2	1.330	1.4619	44.39[14]	8.0861 2597	11.9	23.8
$(C_2H_5)Ge(NCO)_3$	225.4 ± 0.5	−31 ± 2	1.5344	1.4739	41.70[14]	8.4195 2760	12.7	25.3
$Ge(NCO)_4$	204.0 ± 0.4[2]	− 8.0 ± 1.0[2]	1.7714	1.4824	38.77	8.6578 2757[2]	12.6[2]	26.4[2]

Triethylchlorogermane, free from the diethyl and monoethyl derivatives,[10] was prepared in New York: triethylbromogermane, was converted into bis-(triethylgermanium) oxide, and then this was distilled, with collection of a pure center fraction; this pure fraction was then treated with hydrochloric acid, followed by extraction with petroleum ether, by drying and by distillation of solvent.[10]

A 20 volume per cent. solution of each pure ethylchlorogermane, containing 20 g. of the chloride, was changed into the corresponding isocyanate by agency of a 30% excess of silver isocyanate. Ethyltrichlorogermane reacted with such heat as to require gradual addition, while diethyldichlorogermane brought an approximate temperature rise of 30°, and triethylchlorogermane only about 10°. After an hour at 85° and the usual filtration, washing and evaporation of benzene,[1] a nearly 90% yield of crude product resulted. Each individual compound was distilled once in a plain column 4 mm. i. d. and 300 mm. long, with collection of center fractions at the following corrected temperatures: monoisocyanate, 109.4–110.0° at 48 mm.; diisocyanate, 134.5–135.1° at 52 mm.; triisocyanate, 138.4–139.2° at 52 mm.

Chemical Properties of Ethylgermanium Isocyanates.—There is a straight-forward decrease in rate of hydrolysis from germanium tetraisocyanate to the inert tetraethylgermanium; germanium tetraisocyanate hydrolyzes rapidly, with a considerable amount of heat[2]; ethylgermanium triisocyanate also hydrolyzes fairly rapidly, but gives a water-repellent solution; diethylgermanium diisocyanate hydrolyzes at a moderate-to-slow rate; triethylgermanium isocyanate hydrolyzes slowly at 25°, moderately at 55°, and dangerously fast only when shaken with water at 80° or above; tetraethylgermanium does not hydrolyze at 25°. All four isocyanates react with ethanol or butanol-1.

The alcoholysis replaces the isocyanate group with an alkoxy group by a quantitative reaction, as later is shown under Analyses. A similar reaction also has been observed in connection with the fluoroisocyanates of silicon.[17]

Physical Properties of Series (see Table I).—All five compounds are colorless liquids. Both tetraethylgermanium and triethylgermanium isocyanate have weak odors suggesting camphor. Dynamic vapor pressure measurements, made the day after purification, employed a standard method,[15] with apparatus entirely of Pyrex glass and a 250° thermometer, bearing a ground joint, which had been standardized at the boiling points of water and aniline. Errors in temperature could hardly have exceeded 0.4°; moreover, the four new vapor pressure equations predicted the observed points, 760–100 mm., with an average error of approximately 3 mm. or about 1.0%. All three ethylgermanium isocyanates had rather sharp melting points, while the diisocyanate showed a little tendency to supercool. A special 2-ml. micropycnometer served for the densities of all five members of the series.

Germanium tetraisocyanate was prepared freshly and distilled under reduced pressure; tetraethylgermanium was made from tetrachlorogermane and excess ethylmagnesium bromide.

TABLE II

ANALYSES OF ETHYLGERMANIUM ISOCYANATES

Compound	Nitrogen, % Found	Nitrogen, % Calcd.	Mol. wt. (Camphor) Found	Mol. wt. (Camphor) Calcd.	NCO,[16] % Found	NCO,[16] % Calcd.
$(C_2H_5)_3Ge(NCO)$	7.2[a]	6.94	209	201.8	20.7	20.82
$(C_2H_5)_2Ge(NCO)_2$	12.7	13.06	208	214.7	38.9	39.13
$(C_2H_5)Ge(NCO)_3$	18.7	18.45	210	227.7	56.5 54.6	55.36

[a] Performed by students here.

Analyses (see Table II).—A definite volume of each pure liquid at a measured temperature was mixed with a definite volume of butanol-1; the method is chemically similar to that used with the fluoroisocyanates of silicon.[17] Using x in place of 1, 2 or 3 a general equation may be written: $(C_2H_5)_{(4-x)}Ge(NCO)_x + 2x(C_4H_9OH) \rightarrow (C_2H_5)_{(4-x)}Ge(OC_4H_9)_x + x\ NH_2CO_2C_4H_9$. After three days at 20° the nitrogen was determined, as ammonia, by a micro-Kjeldahl method. Professor J. B. Niederl suggested the conversion of carbamate into ammonia.

Slight hydrolysis of the diisocyanate and the triisocyanate accounts for the slightly low molecular weights.

Germanium Tetrachloride and Silver Isothiocyanate.—These reacted neither in benzene nor in nitromethane, a solvent now under investigation; a two-hour test in each case indicated thiocyanuric acid, thiocyanic acid and no volatile germanium tetraisothiocyanate. Thus germanium tetrachloride should be separable from halides which react with silver isothiocyanate, such as boron trichloride,[1] silicon tetrachloride,[7] phosphorus trichloride,[9] sulfur monochloride,[2] sulfuryl chloride[2] and others.

Germanium Tetraisocyanate and Alcohols React.—Unlike germanium tetrachloride or tetrabromide, which do not react, germanium tetraisocyanate reacts vigorously with methanol or ethanol at 25°, after an initial delay of about fifteen seconds. Propanol-1, butanol-1 and *t*-butyl alcohol also react with germanium tetraisocyanate.

Germanium Oxyisocyanate.—Twenty grams of germanium tetrachloride and an excess of silver isocyanate yielded a crude germanium isocyanate, which was distilled with concentration of the yellowish end-fraction first to two ml. and then, in smaller equipment and at two mm. pressure, to one-half ml. This resultant light-medium yellow liquid had the following properties: $d^{17.7}_4$ 1.962; index of refraction 1.5119 at 17.7°; composition, 32.2% Ge; no divalent germanium, blank test with bromine at 100°. All this information is consistent with the existence of a non-volatile germanium oxyisocyanate which is formed by partial hydrolysis of germanium tetraisocyanate, and which is soluble in germanium tetraisocyanate. A sample of very nearly pure germanium tetraisocyanate was allowed to stand open to moist air for two weeks, with a gradual appearance of a yellow color, and with an increase in the index of refraction to 1.4992 at 20°. Thus germanium forms an oxyisocyanate, while several silicon oxyisocyanates are known, in addition to one silicon oxyisothiocyanate.[18] The most probable formula for the dissolved germanium oxyisocyanate is $[GeO(NCO)_2]_n$, corresponding to the known oxychloride, $[GeOCl_2]_n$, which

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[10] Kraus and Flood, THIS JOURNAL, **54**, 1635 (1932).

[11] Kraus and Flood, ref. 10, give 163.5° uncorrected.

[12] Dennis and Hance, THIS JOURNAL, **47**, 370 (1925).

[13] In good agreement with $d^{24.5}_{24.5}$ 0.991, in ref. 12.

[14] Calculated 47.50, 44.59 and 41.68 ml., molar refractions (L. and L.).

[15] Mack and France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 47.

[16] By back-titration of isocyanic acid; use of ethanolic sodium hydroxide, with thymolphthalein as indicator. To be described in a future publication.

[17] Anderson, THIS JOURNAL, **69**, 1241 (1947).

[18] Forbes and Anderson, *ibid.*, **69**, 3048 (1947).

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).