TABLE IV

LIMITING EQUIVALENT CONDUCTANCES AND THERMODYNAMIC DISSOCIATION CONSTANTS OF SULFURIC ACID IN METHANOL

t, °C.	Λ_0	K
20	175.6	0.027
25	186.4	.024[a]
30	196.4	.024
35	208.9	.018

[a] Due to typographical error this value was reported as 0.029 in the first publication.[5]

stant, K. Consequently, the present techniques of conductivity measurements can be used only to determine the order of magnitude of the dissociation constant. A general consistency of the values of K in Table IV is indicated. Electromotive force measurements conducted in this Laboratory may yield more precise values of the dissociation constants of sulfuric acid in methanol.

Summary

Conductance data for dilute solutions of sulfuric acid in methanol are given at 20, 30 and 35°. In general, the data permit the same conclusions that were deduced from earlier measurements at 25°[4]: namely, that sulfuric acid in methanol exhibits properties of a strong univalent electrolyte.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Silicon Methoxyisocyanates. Molar Refractions in Carbon, Silicon and Germanium Compounds Containing Isocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The better to evaluate the properties and functions of cyanate and thiocyanate radicals as pseudohalogens, efforts have been made in this Laboratory to prepare complete series of compounds containing both halogen and pseudohalogen. The only series previously completed has been that of the silicon chloroisocyanates,[1] although compounds formulated as PCl_2NCO,[2] $POCl_2SCN$,[2] $SiCl_3SCN$[2] and presumably $GeCl_3Br$[3] have recently been obtained. The chief difficulty encountered has been the redistribution reaction,[3] which has often proved so rapid that fractional distillations produced mixtures only. Of course the higher boiling intermediates have proved the hardest to isolate. The gaps in the series already blocked out have hampered our efforts to follow trends in physical and chemical properties due to successive substitutions.

The stability of the silicon–oxygen bond suggested an additional approach to the problem. Through the new compounds $Si(OCH_3)_3NCO$, $Si(OCH_3)_2(NCO)_2$ and $Si(OCH_3)(NCO)_3$ a second complete series has now become available. The data already in hand have made possible certain calculations of refraction equivalents as described below. In addition, we have investigated the reactions of silver isocyanate with silicochloroform and hexachlorodisilane, and identified the products.

Preparation of Silicon Methoxyisocyanates.—In view of the success of the hot tube method for obtaining the intermediate members of the silicon chloroisocyanate series,[1] we first passed the mixed vapors of methyl silicate and silicon isocyanate through a tube at 450° (approximately). At a higher temperature methyl silicate becomes unstable. The reaction, if any, at this temperature proved too slow for detection, due perhaps to the stability of the silicon-oxygen bond mentioned above. Therefore a method analogous to one devised by Friedel and Crafts[4] was next employed. A small-scale reaction between silicon isocyanate and methyl alcohol proved vigorous, and gave no immediate precipitate suggestive of silicic acid. Thereupon 40 g. of silicon isocyanate containing 0.82 mole of (NCO) was placed in a 100-cc. flask, and 26 ml. of absolute methyl alcohol (0.65 mole) was added very slowly, with agitation. A solid which gradually settled out was shown to be a polymer of cyanic acid–cyanuric acid or cyamelide. In a second experiment 1.31 mole of isocyanate and 0.49 of the alcohol were combined. After an hour on the steam-bath the volatile products were repeatedly fractionated in a 50-cm. Podbielniak-type column of 6 mm. o. d. with a close-fitting copper spiral. If spaced evenly between the boiling point of methyl silicate, 121°, and that of silicon isocyanate, 186°, the boiling points of the mixed compounds would be 138, 154 and 170°, respectively. We collected them in the (uncorrected) temperature intervals 135.9–136.2°, 150.3–150.6°, and 166.5 to 166.8°. The corrected boiling points are found in Table III.

Analyses.—A preliminary attempt was made to check the composition of the above fractions by direct determination of cyanate. Weighed samples, in 50-ml. conical flasks, were hydrolyzed in dilute sodium hydroxide, and carefully neutralized. Excess of standard silver nitrate was added, and the precipitated silver cyanate filtered off. As the solubility of silver cyanate in pure water is 0.072 g./l. at 19°[5] the washing of the precipitate and paper introduced a serious uncertainty. The results, though mediocre, supported the postulated formulas. For $Si(OCH_3)_3NCO$, (NCO) found was 27.1% and 27.7%, calculated 25.8%; for $Si(OCH_3)_2(NCO)_2$, found 48.2% and 47.0%, calculated 48.3%; for $Si(OCH_3)(NCO)_3$ found 67.1% and 65.3%, calculated 68.1%.

Preliminary microanalyses, by combustion, for carbon, hydrogen and nitrogen in the Converse Laboratory yielded results fairly consistent with theory, in spite of the difficulty of burning the mixed compounds completely in oxygen. The final analyses, performed in a microchemical laboratory elsewhere, appear in Table II. Unfortunately, methoxyl determinations could not be undertaken.

The above report stressed the difficulties encountered

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(1) Anderson, THIS JOURNAL, **66**, 934 (1944).

(2) Anderson, unpublished data.

(3) Forbes and Anderson, THIS JOURNAL, **66**, 931 (1944).

(4) Friedel and Crafts, *Ann. chim.*, [4] **9**, 35 (1866).

(5) Birckenbach and Huttner, *Z. anorg. Chem.*, **190**, 26 (1930).

TABLE I

YIELDS OF SILICON METHOXYCYANATES, G.

Expt.	$\frac{\text{Mols }(OCH_3)}{\text{Mols NCO}}$	$Si(OCH_3)_4$	$Si(OCH_3)_3$-NCO	$Si(OCH_3)_2$-$(NCO)_2$	$SiOCH_3$-$(NCO)_3$	$Si(NCO)_4$	Higher polymers
1	0.79	5	30	2	..	....	25
2	0.37	2	7	35	15	2-3 (?)	17

TABLE II

ANALYSES OF SILICON METHOXYCYANATES

Compound	% Carbon		% Hydrogen		% Nitrogen		M(micro)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Si(OCH_3)_3NCO$	29.11	29.5	5.19	5.52	10.00	8.60	177.179	163.1
$Si(OCH_3)_2(NCO)_2$	27.58	27.6	3.34	3.34	15.72	16.10	177.169	174.3
$Si(OCH_3)(NCO)_3$	25.83	25.9	1.69	1.62	22.57	22.7	187.193	185.1

TABLE III

PROPERTIES OF SILICON METHOXYCYANATES

Compound	B. p., °C.	$d^{20}{}_4$	$n^{20°}$	M/d.	R, ml.
$Si(OCH_3)_4$	121.0 ± 0.5[6]	1.023[8]	1.3683[6]	148.7	33.49
$Si(OCH_3)_3NCO$	137.6 ± .5	1.123	1.3839	145.3	33.95
$Si(OCH_3)_2(NCO)_2$	152.1 ± .5	1.208	1.4028	144.1	35.07
$Si(OCH_3)(NCO)_3$	168.4 ± .5	1.313	1.4287	141.0	36.33
$Si(NCO)_4$	185.6 ± .5	1.442[a]	1.4610	135.9	37.29

[a] Calculated from a new determination, at 25°.

in the analysis. Allowing for these, it would seem that all three compounds are definitely established. Micromolecular weights seldom attain a high degree of accuracy, but these are of the right magnitude, and prove the compounds to be monomeric.

Physical Properties.—The properties, including molar refractions (white light) $R = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{d}$, appear in Table III.

Shortly after recording each boiling point, the thermometer was read, in the same apparatus at the same barometric pressure, close to 760°, with a second pure liquid having a known boiling point close to the first. The difference between the normal boiling points was assumed equal to the difference observed under these identical conditions. Holzapfel,[6] who checked the composition of her methyl silicate by methoxyl determinations and laid much stress on exclusion of moisture so as to avoid hydrolysis followed by loss of water to form $(CH_3O)_3Si—O—Si(OCH_3)_3$, reports 121°, while Kahlenberg and Koenig's[7] best final fraction boiled at 121° at 742 mm.

Densities of the last four compounds were determined using a calibrated 2-ml. bulb with a capillary stem. The spread in reported densities of methyl silicate is excessive. Reduced to 20°, these are 1.023,[8] 1.028,[9] 1.031,[10] 1.036.[8] The scale of our Abbe refractometer was corrected from readings on water and carbon tetrachloride. Hydrolysis due to atmospheric moisture could not be avoided altogether.

Chemical Properties.—All the compounds are hydrolyzed by water at a moderate rate. At first, no silica gel is observed, but this appears in concentrated solutions within a short time. In contrast to the random rearrangement attained by silicon dichlorodiisocyanate in a hot tube at 600°, was the high stability of silicon dimethoxydiisocyanate, the rearrangement of which under the same conditions was too slow for convenient study.

Calculation of Refraction Equivalents. Refraction increment, ($R_{NCO} - R_{OCH_3}$), when both groups are attached to silicon, was found according to Table IV. In view of the uncertainties regarding the physical properties of methyl orthosilicate, the monosubstituted isocyanate was used as a starting point for successive substitutions. $R_{Si(OCH_3)_3(NCO)}$ is designated as R_1 and ($R_{NCO} - R_{OCH_3}$) as R_2.

TABLE IV

EVALUATION OF $R_{NCO} - R_{OCH_3}$

$R_{Si(OCH_3)_2(NCO)_2} - R_1 = R_2 = 35.07 - 33.95 = 1.12$; $R_2 = 1.12$ ml.

$R_{Si(OCH_3)(NCO)} - R_1 = 2R_2 = 36.33 - 33.95 = 2.38$; $R_2 = 1.19$ ml.

$R_{Si(NCO)_4} - R_1 = 3R_2 = 37.29 - 33.95 = 3.34$; $R_2 = 1.11$ ml.

$6R_2 = 6.84$; R_2(av.) $= 1.14$ ml.

Average value of R_{OCH_3} (in carbon compounds)[11] $= 1.64 + 2.42 + 3(1.10) = 7.36$ ml. Approximate value of $R_{NCO} = 7.36 + 1.14 = 8.50$ ml.

To test the constancy of R_{NCO} we have averaged all the data on silicon chloroisocyanates[1]

TABLE V

EVALUATION OF $R_{NCO} - R_{Cl}$

$R_{SiCl_3NCO} - R_3 = R_4 = 31.11 - 28.65^{10,12} = 2.46$: $R_4 = 2.46$ ml.

$R_{SiCl_2(NCO)_2} - R_3 = 2R_4 = 33.34 - 28.65 = 4.69$: $R_4 = 2.345$ ml.

$R_{SiCl(NCO)_3} - R_3 = 3R_4 = 35.31 - 28.65 = 6.66$; $R_4 = 2.22$ ml.

$R_{Si(NCO)_4} - R_3 = 4R_4 = 37.29 - 28.65 = 8.64$; $R_4 = 2.16$ ml. $10R_4 = 22.45$; R_4 (av.) $= 2.25$ ml.

Average value of R_{Cl} (in carbon compounds) $= 5.97$ ml.[11] Approximate value of $R_{NCO} = 5.97 + 2.25 = 8.22$ ml.

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(6) Holzapfel, *Z. Elektrochem.*, **47**, 327 (1941).

(7) Kahlenberg and Koenig, *J. Phys. Chem.*, **12**, 290 (1908).

(8) Sugden and Wilkins, *J. Chem. Soc.*, 126 (1931).

(9) Konrad, Bächle and Signer, *Ann.*, **474**, 276 (1929).

(10) Abati, *Z. physik Chem.*, **25**, 353 (1898).

(11) Eisenlohr, "Spektrochemie organischer Verbindungen," Ferdinand Enke, Stuttgart, 1912, p. 48.

(12) Hölemann, *Z. physik. Chem.*, **B32**, 353 (1936).

after excluding one density for the dichloro compound because of apparent gross error. Averaged densities have been adjusted, to the (averaged) temperatures at which the (averaged) refractive indices were measured, by use of the arbitrary temperature coefficient −0.0015 g./ml./deg. The results appear in Table V, where R_{SiCl_4} is designated as R_3, and (R_{NCO} − R_{Cl}) as R_4.

Discussion.—An interpretation of bond lengths in covalent isocyanates by Eyster, Gillette and Brockway[13] indicates a fractional negative charge upon the nitrogen atom. The bond lengths in silicon tetrachloride indicate substantial ionic as well as double bond character, but silicon tetrabromide should be much more nearly a pure covalent compound.[14] When chlorine atoms are replaced by the less electronegative but presumably more deformable cyanate groups (Table V), R_{NCO} − R_{Cl} decreases. The molar refractions of the chloroisocyanates plotted against the number of isocyanate groups lie on a smooth curve convex upward. Assuming that changes in the R_{Si} are relatively unimportant, there seems to be either a decrease in the molar refraction of isocyanate or an increase in the atomic refraction of chlorine, or both, as the replacement proceeds. Debye[15] has shown that the partially abnormal behavior of molecular polarization in dipole liquids is due to hindrance of free rotation through the influence of neighboring molecules. Hölemann[12] argues that even the medium around symmetrical molecules such as $SiCl_4$ is not truly isotropic. Possibly a part of the variability of R_{NCO} − R_{Cl} could be ascribed to such effects.

The possibility of obtaining from our data a new value for the refraction equivalent of nitrogen (in isocyanates) is obvious, but we refrain from adding to the thirty-odd equivalents already provided by Brühl.[16]

Comparison of Group IVA Compounds.—A further illustration of the effects of successive substitutions of a unit more electronegative and more deformable than the one replaced is afforded by Leithe's[17] molar refractions of chloromethanes and chloroethanes. In calculating R_{Cl} (Table VI) R_C and R_H are always taken as 2.42 and 1.10 ml., respectively,[11] so that all irregularities are attributed to chlorine.

TABLE VI

MOLAR REFRACTIONS OF CHLORO-PARAFFINS

Compound	R compound	R_{Cl}
CH_2Cl_2	16.37	5.88
$CHCl_3$	21.40	5.96
CCl_4	26.31	5.97
C_2H_5Cl	16.18	5.84
CH_3CHCl_2	21.15	6.01

It remains to appraise the influence of carbon, silicon and germanium upon R_{Cl}, R_{NCO} and R_{Br}, respectively. Molar refractions listed in Table VIII which were obtained from the literature are so indicated. In calculating the others from the original data cited in Table VII several densities had to be adjusted to water at 4° or to those temperatures at which the corresponding refractive indices had been measured. When a density was given at one temperature only, an arbitrary coefficient of from −0.0015 to −0.0020 g./ml./deg. was applied over a range never exceeding five degrees. As carbon tetrabromide is a solid at room temperature, its molar refraction was found[17] at 99.5°.

TABLE VII

DENSITIES AND REFRACTIVE INDICES

Compound	d at $t°$	n at $t°$
C_6H_5Cl	$d^{20}{}_4$ 1.106[18]	1.5248 at 20[18]
C_6H_5Br	$d^{20}{}_4$ 1.4914[18]	1.5598 at 20[18]
$SiBr_4$	$d^{23.5}{}_4$ 2.772[10]	1.5627 at 25[10]
$GeCl_4$	$d^{20}{}_{20}$ 1.879[19]	1.4638 at 20°[19]
$Ge(NCO)_4$	$d^{24.5}{}_4$ 1.7647[20]	1.4826 at 22.5[20]
$GeBr_4$	$d^{29}{}_{29}$ 3.1315[21]	1.6269 at 25[21]

TABLE VIII

MOLAR REFRACTIONS OF GROUP IVA COMPOUNDS

Chlorides	R (Chlorides)	Isocyanates	R (isocyanates)	Bromides	R (bromides)
C_6H_5Cl	31.16	C_6H_5NCO[16]	33.91	C_6H_5Br	34.03
CH_3Cl	11.69[a]	CH_3NCO[22]	13.39	CH_3Br	14.58[a]
C_2H_5Cl[17]	16.18	C_2H_5NCO[22]	18.26	C_2H_5Br[17]	19.05
CCl_4[12]	26.47	...	...	CBr_4	38.32[17]
$SiCl_4$[12]	28.65	$Si(NCO)_4$	37.29	$SiBr_4$	40.72
$GeCl_4$	31.68	$Ge(NCO)_4$	38.86	$GeBr_4$	44.74
$SnCl_4$[12]	35.22	...	...	$SnBr_4$[12]	48.73

[a] By summation of atomic refractions observed in liquid carbon compounds.[11]

Our efforts to prepare carbon tetraisocyanate, $C(NCO)_4$, or carbon chloroisocyanates, have as yet proved unsuccessful. Brühl's monumental tables[16] include but one isocyanate (C_6H_5NCO), and this is not altogether suitable for our purposes because of the conjugation which exists in it but not in chlorobenzene or bromobenzene. Methyl chloride and bromide have not been measured in the liquid state. The ethyl compounds thus seem to constitute the only available triad which is free from objections.

Appropriate combinations of the data in Table VIII, including division by four wherever necessary, lead to the second and fourth columns in Table IX. Assuming, for the moment, that R_{Cl} is constant at 5.97 ml., and R_{Br} at 8.87 ml.,

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[13] Eyster, Gillette and Brockway, THIS JOURNAL, **62**, 3236 (1940).

[14] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Chapter VII.

[15] Debye, *Physik. Z.*, **36**, 100 (1935).

[16] Brühl, *Z. physik. Chem.*, especially **79**, 1 (1912).

[17] Leithe, *Z. Elektrochem.*, **37**, 623 (1931).

[18] International Critical Tables, McGraw-Hill Book Co., New York, N. Y., VII, 1930, page 38.

[19] Laubengeyer and Tabern, *J. Phys. Chem.*, **30**, 1048 (1926).

[20] Average of data of Laubengayer and Reggel, THIS JOURNAL, **65**, 1783 (1943); and of Forbes and Anderson, *ibid.*, **65**, 2273 (1943).

[21] Dennis and Hance, *ibid.*, **44**, 299 (1922).

[22] v. Auwers, *Ber.*, **61**, 1041 (1928).

we obtain the values of R_{NCO} in the third and fifth columns.

TABLE IX

$R_{NCO} - R_x$ IN GROUP IV A

Element	$R_{NCO} - R_{Cl}$	R_{NCO}	$R_{Br} - R_{NCO}$	R_{NCO}
Carbon	2.08	8.05	0.84	8.03
Silicon	2.25	8.22	.86	8.01
Germanium	1.79	7.76	1.47	7.40

The relatively small value of $R_{NCO} - R_{Cl}$ in the germanium compounds might be attributed to an excessive polarizing action of germanium atom due to its non-inert gas configuration. Thereby, the more deformable isocyanate group would suffer the more severely. This would be analogous to the shortening of interionic distances in halide crystals when silver ion is substituted for sodium ion.[23] On the other hand, if the data from which we have calculated R_{GeBr_4} are correct, the corresponding $R_{Br} - R_{NCO}$ would demand an abnormal "tightening" of isocyanate by germanium atom for its explanation. Such an effect would be consistent with the small difference between $R_{Si(NCO)_4}$ and $R_{Ge(NCO)_4}$.

Order of Stabilities.—In passing through a hot tube (400–450°), vapors of silicon isocyanate are not perceptibly attacked by oxygen, chlorine or bromine. However, freshly sublimed antimony trifluoride reacts readily with silicon tetrabromide[24] and slowly with silicon tetrachloride.[25] In similar experiments we have noted decreasing reaction rates in the order chloride, isocyanate, bromide. While fully realizing the risks of predicting relative affinities from reaction rates alone we think these observations not inconsistent with bond strengths and electronegativities of halide (or halogenoid) decreasing in the same order.

Reactions of Silver Isocyanate with Silicochloroform and Hexachlorodisilane

The ready replacement of one or more chlorine atoms in silicon tetrachloride by cyanate groups prompted efforts to prepare corresponding derivatives from $SiHCl_3$ and Si_2Cl_6. These substances were available, by exchange, through the courtesy of Professor W. C. Schumb of the Massachusetts Institute of Technology.

In 100 ml. of benzene, 13.5 g. of silicochloroform was treated with excess (60 g.) of silver isocyanate. Products obtained were free silicon, and 9 g. of crude silicon isocyanate which contained about three per cent. of silicon cyanate. The fate of the hydrogen is unknown. Lead cyanate gave similar results.

To 10 ml. of hexachlorodisilane dissolved in 100 ml. of benzene 60 g. of silver isocyanate was slowly added. A vigorous reaction ensued, and produced a solid quite dark in appearance. Several experiments were performed, one in 500 ml. of benzene. The products in all cases included silicon isocyanate and cyanate in the surprisingly low ratio four to one, plus elementary silicon. When lead cyanate was used, the reaction was less vigorous, and a colorless product was obtained which decomposed when attempts were made to distill it under vacuum. It is proposed to repeat this experiment, in the hope of isolating pure hexaisocyanatodisilane, $Si_2(NCO)_6$, by fractional freezing, or by suitable choice of solvent.

Summary

1. Silicon isocyanate reacts with methyl alcohol at room temperature to form a mixture of the (new) silicon methoxyisocyanates, $Si(OCH_3)_3(NCO)$, $Si(OCH_3)_2(NCO)_2$, $Si(OCH_3)(NCO)_3$ as well as methyl silicate $Si(OCH_3)_4$. All these compounds are fully stable and can be completely separated by fractional distillation. Even at 450° rearrangements are slow.

2. Boiling points, densities and refractive indices have been measured. Molar refractions have been evaluated, and compared with those in the silicon chloroisocyanate series.

3. Assuming for the sake of argument that R is constant for all other atoms present, the average R_{NCO} is found to be 8.50 ml. in the silicon methoxyisocyanate series and 8.22 ml. in the silicon chloroisocyanate series.

4. Considering carbon, silicon and germanium compounds in this order, $R_{NCO} - R_{Cl}$ and $R_{Br} - R_{NCO}$ increase. Irregularities in these progressions are discussed.

5. Reaction rates of antimony fluoride with silicon tetrachloride, isocyanate and bromide decreasing in this order are not inconsistent with a corresponding order of bond strengths and of electronegativities.

6. Both silicochloroform and hexachlorodisilane, upon reaction with silver isocyanate in benzene, yield silicon isocyanate, silicon cyanate and free silicon.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 16, 1944

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[23] Fajans, *J. Chem. Phys.*, **9**, 281 (1941).

[24] Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

[25] Booth and Swinehart, *ibid.*, **57**, 1333 (1935).