lytically from $M = 0$ to $M = 0.001$, assuming that Δj is proportional to M. For the more concentrated solutions, the evaluation is carried out graphically. Table III contains the provisional activity coefficients for the four salts at rounded concentrations.

TABLE III

VALUES OF THE ACTIVITY COEFFICIENT, γ', FOR THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Molality	Lim. law	$Ba(ClO_4)_2$	$Sr(ClO_4)_2$	$Ca(ClO_4)_2$	$Mg(ClO_4)_2$
0.001	0.910	0.895	0.897	0.897	0.898
.002	.841	.858	.861	.861	.861
.005	.760	.798	.802	.803	.803
.01	.678	.743	.750	.751	.752
.02	.577	.682	.695	.697	.697
.05	.420	.599	.625	.629	.628
.1	.293	.540	.579	.587	.588
.2	.176	.489	.546	.566	.578
.3	.119	.463	.533	.572	.591
.4	.086	.450	.545	.589	.619
.5	.064	.443	.556	.615	.655
.6		.441	.572	.646	.698
.7		.440	.592	.683	.749
.8		.442	.615	.725	.807
.9		.446	.642	.774	.872
1.0		.451	.673	.834	.947

Discussion of Results

It is believed that most of the freezing point data obtained in this investigation are accurate to within 0.05–0.10% of the freezing point depression. In the analysis of the equilibrium solutions, the mean deviation of three or four determinations was consistently in the range 0.03–0.05%.

Values of the activity coefficients for magnesium perchlorate[6] in the literature were obtained by the isopiestic method. The differences between these data and those of the present investigation are within the range of the experimental error.

No attempt has been made to correlate the differences of activity coefficients with the size and shape of ions.

Acknowledgment.—This work was made possible, initially, by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Bureau of Ordnance, Navy Department, Contract NO rd-9195 and, during the year 1949–1950, by the award of a fellowship from the Humble Oil and Refining Company, Houston, Texas.

Summary

1. The freezing point depression method was used to determine the activity coefficients of the alkaline earth and magnesium perchlorates in aqueous solutions over a concentration range 0.003 to 1 molal.

2. The activity coefficients were calculated from j-values listed for rounded concentrations.

3. The activity coefficients are based upon freezing point data accurate to within 0.05 to 0.10% of the observed depression and upon concentration determinations consistent to within 0.03–0.05%.

[6] Stokes and Levien, THIS JOURNAL, **68**, 333 (1946).

AUSTIN, TEXAS RECEIVED MARCH 25, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Electric Moments of Organosilicon Compounds. I. Fluorides and Chlorides[1]

BY COLUMBA CURRAN, ROBERT M. WITUCKI AND PATRICK A. MCCUSKER

The availability of d orbitals for bond formation in elements of the sodium series suggests a potential double bond character in silicon compounds which is not possible in carbon compounds. Contributions of structures containing double bonds are generally more common in elements of the sodium series than in elements of the potassium series. Brockway and Coop[2] have studied the bond character in the chlorosilanes by means of electron diffraction and electric moment measurements. The low moments for these compounds, SiH_3Cl 1.28, SiH_2Cl_2 1.17 and $SiHCl_3$ 0.85, compared to the values for the chloromethanes CH_3Cl 1.87, CH_2Cl_2 1.56 and $CHCl_3$ 1.00, were interpreted by these workers as suggesting contributions of structures of the type $H_3^{-}Si{=}Cl^{+}$ to the chlorosilane molecules. This double bond character of the silicon-to-chlorine bond is further indicated by the relatively large moments of the corresponding germanium compounds.[3]

Sauer and Mead[4] have reported a moment of 0.74 D for hexamethyldisiloxane. In calculating the oxygen valence angle in this compound, these authors neglected potential double-bond character and assumed a Si–C bond moment of 1.0, with the carbon the negative end of the dipole, and a Si–O bond moment of 2.8. More recently Wright and Hunter[5] have reported the infrared spectra of the methylpolysiloxanes. The intensity of the absorption peak attributed to the Si–O stretching vibration was observed by these workers to be about five times as great as that for the C–O bond in ethers. They interpreted this high intensity as due to a large degree of ionic

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[1] Presented at the New York Meeting of the American Chemical Society, September, 1947.

[2] Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

[3] Smyth, THIS JOURNAL, **63**, 57 (1941).

[4] Sauer and Mead, *ibid.*, **68**, 1794 (1946).

[5] Wright and Hunter, *ibid.*, **69**, 803 (1947).

character in the Si–O bond. The strong absorption attributed to the Si–C stretching vibration was interpreted as an indication of a large $^+$Si–C$^-$ dipole and the low intensity of the C–H absorption as an indication of the low polarity of the C–H bonds resulting from a charge migration from silicon to carbon. These interpretations appeared to us to be inconsistent with the moments reported for the halosilanes. In order to obtain more pertinent data on the charge distribution in organosilicon compounds we have determined the electric moments of some alkyl- and arylhalosilanes.

Experimental

Preparation and Purification of Compounds.—Ethyltrichlorosilane and diethyldichlorosilane were obtained from Dow–Corning and were purified by fractional distillation in a 53-inch, glass helix packed column. The purified liquids had the properties: ethyltrichlorosilane, b. p. 100–100.1 at 746 mm., d^{24}_4 1.2342; diethyldichlorosilane, b. p. 129.0 at 744 mm., n^{25}_D 1.4291, d^{25}_4 1.0472.

Triethylchlorosilane was prepared by the reaction of ethylmagnesium bromide with diethyldichlorosilane and purified by fractional distillation in the 53 in. column. The product obtained had the following properties: b. p. 145.8–146.0, n^{25}_D 1.4299. Phenyltrichlorosilane was prepared by the reaction of silicon tetrachloride with phenylmagnesium chloride and the product obtained was purified by fractional distillation. The purified material boiled at 85.1° at 15 mm. The purity was checked by analyzing for chloride by titration of an aqueous suspension with standard base.

Diphenyldichlorosilane and triphenylchlorosilane were obtained from Anderson Laboratories, Adrian, Michigan, and were purified by fractional distillation. The samples used for measurements had the following properties: diphenyldichlorosilane, b. p. 126.0 at 3 mm., n^{25}_D 1.5778 and d^{25}_4 1.20214; triphenylchlorosilane, b. p. 156° at 1 mm., m. p. 94–95°.

Triethylfluorosilane, diethyldifluorosilane, triphenylfluorosilane, diphenyldifluorosilane and phenyltrifluorosilane were all prepared by the reaction of anhydrous zinc fluoride on the corresponding chlorine compounds and were purified by fractional distillation. The purified fluorine compounds had the following properties: triethylfluorosilane, b. p. 109.2°, n^{25}_D 1.3879, d^{25}_4 0.8326; diethyldifluorosilane, b. p. 62.0°, phenyltrifluorosilane, b. p. 101.9°,

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AT 25°

C_2	ϵ	d
	Triethylchlorosilane	
0.00000	2.276	10.8737
.01113	2.339	.8739
.01461	2.359	.8740
.01720	2.374	.8741
	Diethyldichlorosilane	
0.00000	2.276	0.8737
.01339	2.379	.8772
.01786	2.413	.8785
.01908	2.422	.8788
	Ethyltrichlorosilane	
0.00000	2.276	0.8740
.00562	2.307	.8766
.01259	2.345	.8802
.02052	2.388	.8841
	Diphenyldichlorosilane	
0.00000	2.276	0.8736
.00726	2.347	.8792
.00790	2.353	.8793
.01126	2.388	.8819
	Phenyltrichlorosilane	
0.00000	2.276	0.8735
.00906	2.351	.8804
.01716	2.418	.8868
.02206	2.459	.8904
	Triethylfluorosilane	
0.00000	2.276	0.8735
.01245	2.320	.8724
.01784	2.340	.8721
.01789	2.340	.8720
	Diethyldifluorosilane	
0.00000	2.276	0.8737
.01125	2.347	.8747
.01459	2.368	.8749
.02224	2.417	.8755
	Diphenyldifluorosilane	
0.00000	2.276	0.8736
.00816	2.353	.8781
.00833	2.355	.8781
.01098	2.380	.8797
.01358	2.402	.8815
	Phenyltrifluorosilane	
0.00000	2.276	0.8737
.01170	2.395	.8790
.01286	2.407	.8795
.01879	2.466	.8822
	Triphenylchlorosilane	
0.00000	2.276	0.8727
.00887	2.344	.8799
.01176	2.364	.8822
.01535	2.395	.8849
	Triphenylfluorosilane	
0.00000	2.276	0.8728
.01238	2.347	.8815
.01456	2.359	.8830
.01738	2.375	.8851

TABLE II

POLARIZATIONS AND ELECTRIC MOMENTS

	P_2	MR_D	μ
Triethylchlorosilane	134	43.5	2.07
Diethyldichlorosilane	158	38.68	2.39
Ethyltrichlorosilane	121	33.85	2.04
Triphenylchlorosilane	188	89.4	2.14
Diphenyldichlorosilane	207	69.2	2.56
Phenyltrichlorosilane	170.4	48.94	2.41
Triethylfluorosilane	100.5	38.04	1.72
Diethyldifluorosilane	132.4	27.8	2.23
Triphenylfluorosilane	157.2	83.7	1.84
Diphenyldifluorosilane	196	57.8	2.57
Phenyltrifluorosilane	190.4	31.9	2.77

diphenyldifluorosilane, b. p. 93.5–94.0° at 3 mm., n^{25}_D 1.5221, triphenylfluorosilane, b. p. 162–165° at 3 mm. The triphenylfluorosilane was further purified by several recrystallizations from dry ether, m. p. 61.5°.

Measurements and Calculations.—The measurement[6] of dielectric constants and densities and the calculation[7] of electric moments have been previously described. The molar refractions of the diethyldichlorosilane and triethylfluorosilane were obtained from the refraction and density data, and the values for the other compound were taken from or calculated from the data and bond refractions listed by Warrick.[8]

Discussion

The moment obtained for triethylchlorosilane agrees with the value reported for this compound by Malatesta and Pizzotti.[9] The large moments of the organohalosilanes compared to the values for the chlorosilanes reveal that the ethyl and phenyl groups are much more positive with respect to silicon than is hydrogen, on contrast to the interpretations of Wright and Hunter[5] and the assumptions of Sauer and Mead.[4] This polarity suggests a hyperconjugation effect with contributions of such structures as $H^+C{=}Si^-{-}Cl$ and $H^+C{=}SiCl^-$ to the ethylchlorosilanes. The increase in moment from chlorosilane to triphenylchlorosilane, 0.86, compares to an increase of 0.32 from chlorogermane to triphenylbromogermane,[3] indicating, as expected, less double bond character in carbon-to-germanium bonds.

The moments obtained for the silicon compounds investigated along with the values for a few corresponding carbon compounds reported by other investigators are listed in Table III.

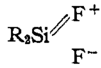
TABLE III

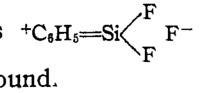
ELECTRIC MOMENTS IN DEBYE UNITS

$(C_2H_5)_3SiCl$	2.07	$(CH_3)_3CCl$	2.15
$(C_2H_5)_2SiCl_2$	2.39	$(CH_3)_2CCl_2$	1.99
$C_2H_5SiCl_3$	2.04	CH_3CCl_3	1.6
$(C_6H_5)_3SiCl$	2.14	$C_6H_5CH_2Cl$	1.85
$(C_6H_5)_2SiCl_2$	2.56	$(C_6H_5)_2CCl_2$	2.39
$C_6H_5SiCl_3$	2.41	$C_6H_5CCl_3$	2.04
$(C_2H_5)_3SiF$	1.72	$C_2H_5(CH_3)_2CF$	1.92
$(C_2H_5)_2SiF_2$	2.23	....	..
$(C_6H_5)_3SiF$	1.84	$C_6H_5CH_2F$	1.77
$(C_6H_5)_2SiF_2$	2.57	....	..
$C_6H_5SiF_3$	2.77	$C_6H_5CF_3$	2.56

The moments of benzotrichloride and benzotrifluoride are the values reported by Freiser, Hobbs and Gross[10] and the value for *t*-amyl fluoride is that of Rogers.[11] Values for the other carbon compounds listed were taken from Technical Report No. II, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1947.

The moments of the chloroalkanes, chloromethanes and chlorosilanes all show the characteristic decrease from the mono- to the trichlorides, attributed to the inductive effect. Diethyldichlorosilane, on the contrary, has a larger moment than the triethylchlorosilane, and the increase is almost exactly that calculated in the absence of an inductive effect. This increase reveals that the R_2Si group is much more polarizable than the H_2C, H_2Si or R_2C groups, suggesting an increased contribution of the structure $H^+C{=}Si^-$ in diethyldichlorosilane.

The moment of triethylfluorosilane is much smaller than the value for the corresponding chloride, whereas the increase in moment from the mono- to the dihalide is much greater for the fluoro compounds. This is consistent with a larger contribution of $R_3^-Si{=}F^+$ than $R_3^-Si{=}Cl^+$ as expected from considerations of the relative tendencies of chlorine and fluorine to form double bonds, and suggests that the introduction of the second fluorine atom in the molecule results in the contribution of the structure  $R_2Si\begin{smallmatrix}{/\!\!/}F^+\\ F^-\end{smallmatrix}$. We were unable to obtain a reliable value for the moment of ethyltrifluorosilane (b. p. −4°) in benzene, but it appears to be at least as large as the moment of the difluoride, in contrast to the decrease observed for moment of the trichloro compound. Unfortunately the moments of the di- and trifluoroalkanes are not available for comparison.

The phenylhalosilanes all have appreciably larger moments than the corresponding carbon compounds. The chloro compounds show a maximum moment for the phenyldichlorosilane, whereas phenyltrifluorosilane has the largest moment of all the compounds investigated, indicating large contributions of such structures as  $^+C_6H_5{=}Si\begin{smallmatrix}F\\ F\end{smallmatrix}\ F^-$ and $^+C_6H_5{=}Si^-F_3$ to this compound.

The moments reported[12] for the parasubstituted trimethylsilylbenzenes reveal that in these compounds the methyl groups are more positive with respect to silicon than is the phenyl group. In the organohalosilanes, particularly in the trihalo compounds, the phenyl group releases electrons to silicon more readily than does the ethyl group, indicating a highly polarizable $C_6H_5{-}Si$ bond.

The moments of the halosilanes, the organohalosilanes and hexamethyldisiloxane indicate that the polarity of the silcon-to-oxygen bond is much less than that assumed by Sauer and Mead.[4] This bond should have appreciable $^-Si{=}O^+$ character. It is planned to investigate the polarity of the Si–O bond in this Laboratory.

Summary

Electric moments have been determined for the three ethylchlorosilanes, the three phenylchlorosilanes, the three phenylfluorosilanes, and for triethylfluorosilane and diethyldifluorosilane.

A comparison of the moments of the ethyl-

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[6] Moede and Curran, THIS JOURNAL, **71**, 852 (1949).

[7] Curran and Chaput, *ibid.*, **69**, 1134 (1947).

[8] Warrick, *ibid.*, **68**, 2455 (1946).

[9] Malatesta and Pizzotti, *Gazz. chim. ital.*, **73**, 143 (1943).

[10] Freiser, Hobbs and Gross, THIS JOURNAL, **71**, 111 (1949).

[11] Rogers, *ibid.*, **69**, 457 (1947).

[12] Roberts, McElhill and Armstrong, *ibid.*, **71**, 2923 (1949).

halosilanes with the values for the chlorosilanes reveals that the ethyl group is much more positive with respect to silicon than is hydrogen. This is interpreted as a hyperconjugation effect. Replacement of an ethyl by a phenyl group results in an increase in moment for all compounds studied. The alkyl- and phenylsilyl groups are more polarizable than the corresponding hydrocarbon radicals.

NOTRE DAME, INDIANA RECEIVED JANUARY 19, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments of Five of the Isomeric Hexachlorocyclohexanes

BY EDWARD L. LIND,[1] MARCUS E. HOBBS AND PAUL M. GROSS

Recent interest in the γ-isomer of hexachlorocyclohexane as an insecticide has given renewed impetus[2] to investigations of the structure of cyclohexane derivatives. The hexachlorocyclohexane molecule affords an unusual opportunity in this connection and, at the same time, structural characterization of its geometric isomers is of considerable interest for the general problem of relating molecular structure and insecticide toxicity. The present investigation is concerned with the determination of the electric moments of the α, β, γ, δ and ε isomers of hexachlorocyclohexane. The values obtained resolve some conflicting statements in the literature and provide information which, along with other types of data, help in the elucidation of the structure of the isomers studied.

Experimental

Solvents.—Thiophene-free benzene (Jones and Laughlin reagent grade) which had been stored over sodium was refluxed and distilled over fresh sodium through a 2-meter Dufton column immediately before use. The middle fraction, distilling over a range of 0.02° or less, was collected with precaution to prevent absorption of atmospheric moisture.

1,4-Dioxane (Carbide and Carbon Chemical Corp., C. P. grade) was refluxed over solid potassium hydroxide until a brown precipitate no longer separated on addition of fresh potassium hydroxide. After distillation from the potassium hydroxide, this aldehyde-free dioxane was refluxed with hydrochloric acid as described by Fieser.[3] This was followed by distillation from potassium hydroxide and two distillations from sodium. The second distillation from sodium was a fractionation in a 2-meter Dufton column. The middle fraction with a distilling range of 0.06° or less was collected with precautions to prevent absorption of atmospheric moisture.

Solutes.—The samples of α, β, γ and δ-hexachlorocyclohexane were separated from the crude mixture of isomers using a procedure developed from the method outlined by Slade.[2]

α-Hexachlorocyclohexane was separated from the commercial grades of hexachlorocyclohexane supplied by the Hooker Electrochemical Company. This was recrystallized four times from acetone.[4] The product was recrystallized once from chloroform and 4 times from benzene, m. p. 156.5–157.0°.

The sample of β-isomer was separated from the mixture of isomers prepared by the chlorination of benzene as described by van der Linden.[4] After one recrystallization from methyl acetate, two from 1,4-dioxane and two from benzene a product with a m. p. of 308–309° was obtained. The product showed no detectable pleochroism when examined with a polarizing microscope. The β-isomer is the only reported isomer of hexachlorocyclohexane with a cubic crystal structure.[5] Only a very faint trace of chloride ion was observed in an alcoholic potassium hydroxide solution of the β-isomer after eight hours at 25°. The β-isomer is the only isomer of hexachlorocyclohexane reported to be stable under these conditions.[6]

A sample of γ-isomer[7] was separated from commercial grade hexachlorocyclohexane supplied by the Hooker Electrochemical Company. This was combined with a sample of γ-isomer obtained from E. I. du Pont de Nemours Co. which had been recrystallized from chloroform to the same melting point. The combined sample was recrystallized twice from chloroform, once from carbon tetrachloride and twice from benzene, m. p. 111.5–112.0°.

δ-Hexachlorocyclohexane was separated from the commercial grade mixture of isomers supplied by the Westvaco Chlorine Products Corp., Commercial Solvents Corporation and by E. I. du Pont de Nemours and Co. This was recrystallized twice from carbon tetrachloride and 3 times from benzene, m. p. 136–137°. The sample used for the measurements in benzene was recovered for the measurements in 1,4-dioxane. Disagreement with previous measurements warranted characterization of the sample used in this investigation. Mixed melting points over a range of composition with samples of δ-isomer obtained from the Dow Chemical Co. and the U. S. Department of Agriculture showed no melting point depression. Each of the three δ-isomer samples was found to give the same melting point depression for the same composition of a mixture of α- and δ-isomers. A different but constant melting point depression was observed for the same composition of a mixture of α- and δ-isomers. The refractive indices of the three δ-samples at 145° were found to be approximately 1.513. The solubility of the δ-isomer used in this investigation was determined in ethanol and found to be in reasonable agreement with the high solubility of the δ-isomer reported by Slade.[2] The sample of δ-isomer obtained from the U. S. Department of Agriculture was used to check the measurements in this investigation since the sharp melting point indicated high purity. It was used with no treatment other than drying *in vacuo* over phosphorus pentoxide, m. p. 137.5–138°.

A small amount of ε-hexachlorocyclohexane was borrowed from the Dow Chemical Co. and recrystallized twice from benzene, m. p. 216.5–218°. The ε-isomer

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(1) Part of the thesis of Edward L. Lind submitted in partial fulfillment of the requirements of the M.A. degree in Chemistry at Duke University, June, 1948.

(2) R. E. Slade, *Chem. and Ind.*, 314 (1945).

(3) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 369.

(4) The ratio of α and β solubilities in acetone is unfavorable for the formation of the eutectic of α and β isomers shown to exist by van der Linden, *Ber.*, **45**, 231 (1912).

(5) L. W. Daasch, *Anal. Chem.*, **19**, 779 (1947).

(6) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

(7) Obtained from a methanol solution as described by Slade.[2] A considerable purification was effected by dissolving the crude γ-isomer in chloroform, filtering from the small amount of β-isomer and adding an equal volume of isopropyl alcohol. The purified γ-isomer was found to precipitate from this solution on standing.