[NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS, LEWIS FLIGHT PROPULSION LABORATORY]

Dielectric Properties of Some Alkylsilanes

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The dielectric constants and refractive indices at three wave lengths have been measured for tetramethyl-, diethyl-, triethyl-, tetraethyl-, dimethyldipropyl-, *n*-butyl- and isobutylsilane. The molar refractions and atomic polarizations have been computed and the dipole moments (of the polar silanes) have been calculated from the Onsager and Kirkwood equations. The following bond moments have been estimated from available data: $\overrightarrow{\overset{-}{\mathrm{H}}\text{–}\overset{+}{\mathrm{Si}}} = 1.0\ D$, $\overrightarrow{\overset{-}{\mathrm{R}}\text{–}\overset{+}{\mathrm{Si}}} = 0.2\ D$, $\overrightarrow{\overset{-}{\mathrm{C}}(\mathrm{sp}^3)\text{–}\overset{+}{\mathrm{H}}} = 0.4\ D$, and $\overrightarrow{\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{Si}}} = 0.6\ D$.

Very few measurements of dipole moments of alkylsilanes[1-3] and only one measurement of the dielectric constant of the pure liquids[4] have been made. It was considered of some interest to measure these quantities for several alkylsilanes. The dielectric constants and refractive indices at three wave lengths were determined for *n*-butyl-, isobutyl-, diethyl, triethyl-, tetraethyl-, tetramethyl- and dimethyldipropylsilane at 20°. The atomic polarizations of these alkylsilanes have been calculated. The dipole moments of diethyl-, *n*-butyl-, isobutyl- and triethylsilane were also calculated by use of the Onsager and Kirkwood equations. The Si–H, Si–R and Si–C bond moments were evaluated.

Experimental

Materials.—The alkylsilanes were prepared and purified at the Lewis Laboratory.[5] These compounds were refractionated through a three-foot vacuum-jacketed column packed with 1/4" stainless steel saddles. The material was finally percolated through a two-foot column packed with alumina and maintained in an inert atmosphere.

Dielectric Constants.—A dielectric constant cell of 25-cc. capacity was used. It was designed so as to make it possible to determine dielectric constants in an inert atmosphere in order to prevent oxidation and hydrolysis of the silanes. The cell was filled in a dry-box containing a nitrogen atmosphere. The dielectric constants were measured at 20.0 ± 0.1° with a probable accuracy of ±0.2%. The dielectric constant apparatus has been previously described.[6] (The conductivities of the alkylsilanes were $\sim 10^{-12}$ mho/cm. These values were close to the bridge limit for resistance of $0.2 \times 10^{+12}$ ohm/cm.)

Indices of Refraction.—The refractive indices were measured with a Bausch and Lomb precision Abbe refractometer enclosed in a dry-box with a nitrogen atmosphere at 20.0 ± 0.1° with an estimated accuracy of ±0.0001. The sodium D(5893 Å.), the mercury $\mathrm{Hg_g}$(5460.7 Å.), and the mercury $\mathrm{Hg_{b.v.}}$4358.3 Å.) lines were used.

Boiling Points.—An ebulliometer[7] equipped with a platinum resistance thermometer was used. The measurements were made in a nitrogen atmosphere with an accuracy of ±0.1°.

Results and Discussion

The values of the boiling points, dielectric constants and refractive indices at 20° are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF ALKYLSILANES

Compounds	B.p., °C. (760 mm.)	ϵ^{20}	$n^{20}\mathrm{D}$	$n^{20}\mathrm{Hg_g}$	$n^{20}\mathrm{Hg_{b.v.}}$
$(CH_3)_4Si$	26.6	1.921[a]	1.3588	1.3605	1.3681
$(C_2H_5)_2SiH_2$	55.8	2.544	1.3917	1.3936	1.4021
$(C_2H_5)_3SiH$	108.7	2.323	1.4120	1.4138	1.4223
$(C_2H_5)_4Si$	153.8	2.090	1.4269	1.4293	1.4375
n-$C_4H_9SiH_3$	56.7	2.537	1.3927	1.3950	1.4036
i-$C_4H_9SiH_3$	48.2	2.497	1.3879	1.3900	1.3986
$(CH_3)_2Si(C_3H_7)_2$	141.7	2.054	1.4145	1.4164	1.4248

[a] Baker, *et al.*,[4] give $\epsilon^{25} = 1.91$ for tetramethylsilane.

The boiling points and refractive indices, n_D, determined in this investigation are generally in satisfactory agreement with the values previously given.[5] The boiling point for tetramethylsilane of 26.6° was determined directly in the present investigation, while Tannenbaum, *et al.*, determined the boiling point by means of an extrapolation of the vapor pressure data. The value of the dielectric constant of tetramethylsilane reported in the present work is in agreement with the value previously reported,[4] taking into consideration the difference in temperature.

Calculation of Dipole Moments.—The refractive indices were extrapolated by least squares to infinite wave length by means of the Cauchy equation. Using these n_∞ values and the densities reported by Tannenbaum, *et al.*,[5] the R_∞ values were calculated from the Lorentz–Lorenz equation. The values of n_∞ and R_∞ found for the three tetraalkylsilanes agree with those obtained by Bygdén[8] (using the D, H_α, H_β, H_γ lines) to about 0.0002 unit in n_∞ and 0.05 cc. in R_∞. The atomic polarization, P_A, was determined for the three non-polar tetraalkylsilanes, by taking the difference between the polarization, P_CM, obtained from the Clausius–Mosotti equation, and R_∞. An empirical relationship between P_A and c, the number of carbon atoms, may be expressed by the linear equation $P_\mathrm{A} = 2.64 + 0.065c$.

In order to calculate accurately dipole moments (where $\mu < 1\ D$) by means of the Onsager equation, an effective refractive index, n_eff, which includes the infrared contribution, must be evaluated. The quantity n_eff^2 is equal to $(2R + V)/(V - R)$, (from

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TABLE II

REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS OF SOME ALKYLSILANES

Silane	n_∞	R_∞, cm.^{3}	P_{CM}, cm.^{3}	P_A, cm.^{3}	ΣP_B, cm.^{3}	n^2_{eff}	μ_1, D	$g^{1/2}\mu_2$, D
Tetramethyl	1.3474	29.34	32.24	2.90	..	1.921[c]	0[d]	0[d]
Tetraethyl	1.4144	47.10	50.19	3.09	..	2.090[c]	0[d]	0[d]
Dimethyl-dipropyl	1.4019	50.70	50.70	3.22[a]	..	2.054[a,c]	0[a]	0[a]
Diethyl	1.3790	29.83	...	2.90[b]	2.58	2.006	0.76 (0.75)[e]	0.87 (0.86)[e]
n-Butyl	1.3797	30.09	...	2.90[b]	2.43	2.001	.76 (.75)[e]	.87 (.86)[e]
Isobutyl	1.3750	29.90	...	2.90[b]	2.43	1.987	.75 (.73)[e]	.86 (.84)[e]
Triethyl	1.3993	38.45	...	3.03[b]	2.88	2.055	.60 (.59)[e]	.76 (.75)[e]

[a] Owing to slight differences in the induced moments of the methyl and propyl groups, dimethyldipropylsilane may have a very small moment. The difference of 0.13 cm.^{3} between tetraethylsilane and dimethyldipropylsilane may be ascribed to this very small moment or just to experimental error. Omission of the P_A value for this compound would not affect the evaluation of P_A or P_B appreciably. [b] Obtained from empirical equation, $P_A = 2.64 + 0.065\,c$. [c] For the non-polar tetra-alkylsilanes, $\epsilon = n^2_{eff}$. [d] From molecular symmetry considerations. [e] Moments calculated using n^2_{eff} obtained from P_A values given by empirical equation.

the Lorentz–Lorenz equation) where $R = R_\infty + P_A$ and V is the molar volume.

Two methods may be used to calculate the atomic polarization. First, the atomic polarization can be evaluated for the polar alkylsilanes from the empirical relationship between P_A and c found for the non-polar silanes. This is equivalent to assigning P_A contributions to the individual atoms C, Si and H. It is important to note, however, that the polar and non-polar silanes with the same number of C, Si and H atoms do not have the same number of C–H, Si–C, etc., bonds. Since the atomic polarization is associated with bond vibrational frequencies,[9-12] the use of a relationship applicable to one bonding type to obtain a value for a second bonding type may be rather unsatisfactory.

The second empirical method available to determine the atomic polarization is to obtain what may be termed bond polarizations, P_B, and sum the P_B values for a particular compound. Audsley and Goss[13] found $P_A = 0.08$ cc. for gaseous methane and a CH_2 increment of 0.07 cc. These values give P_B(C–H) = 0.02 cc. and P_B(C–C) = 0.03 cc. Using these values along with P_A for the liquid tetralkylsilanes, and using an approximate field anisotropy correction[13] from the alkanes given by $X = 0.21 + 0.006c$, a value for P_B(Si–C) of 0.60 cc. is obtained. Since $P_A = 1.76$ cc. for SiH_4,[14] P_B(Si–H) is equal to 0.44 cc. These P_B values are summed up to give ΣP_B for each of the polar alkylsilanes. The values of P_A and ΣP_B are given in Table II.

The values for P_B obtained were used to calculate the values of n_{eff}, μ_1 and $g^{1/2}\mu_2$ given in Table II, where μ_1 is the Onsager moment,[15] and $g^{1/2}\mu_2$ is calculated from the Kirkwood equation.[16,17] However, the values obtainable for μ_1 and $g^{1/2}\mu_2$ by using the first method to calculate P_A values are also given in parentheses.

From a study of the Stark effect on the microwave absorption spectrum of CH_3SiH_3, a dipole moment of 0.73 D was calculated.[3] The moments of *n*-butyl- and isobutylsilane would be expected to be slightly larger than that of methylsilane owing to the additional induced moments and to increased availability of electrons from the alkyl groups. Thus the values of 0.86–0.87 D and 0.75–0.76 D calculated from the Kirkwood and Onsager equations, respectively, for the butylsilanes are quite reasonable.

From dilute solution measurements in carbon tetrachloride[1] and benzene,[2] moments of 0.72 and 0.75 D, respectively, for triethylsilane were reported. The value of 0.60 D obtained from the Onsager equation in this investigation is somewhat lower, but the moment calculated from the Kirkwood equation, 0.76 D, is in good agreement.

The dipole moment of diethylsilane has not been previously reported but the values of 0.76 and 0.87 D from the Onsager and Kirkwood equations, respectively, appear satisfactory.

Calculation of Bond Moments.—Bond moments of 0.3 D for Si–H and 0.7 D for C–Si have been assigned[2] on the basis of electronegativity differences. However, recent theoretical considerations of the bond moments of molecules,[18-20] indicate that the bond moment is not simply related to electronegativity or ionic character. Not only must the ionic moment be considered but also the homopolar or overlap moments[20] and the hybridization or atomic moment[18-20] must also be considered in detail. It would seem useful, therefore, to approach the problem by application of information as to bond moments gained from infrared intensity measurements.

It would be desirable first to estimate the $\underset{-\ \ +}{\overrightarrow{\text{Si–H}}}$ bond moment. A bond moment for F–Si in SiF_4 of 2.3 D has been obtained from infrared absorption measurements.[21] Furthermore, from measurements of the Stark effect on microwave absorption spectra, dipole moments[14] have been obtained for $SiHF_3$ of 1.26 D and for SiH_3F of 1.268 D. If

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(9) The term atomic polarization is a somewhat unfortunate choice, *e.g.*, vapors of atomic species such as the inert gases and Hg have no atomic polarization (see ref. 14). This particular portion of the polarization is more correctly associated with the bending and stretching vibrations between atoms and perhaps should be termed total bond polarization rather than atomic polarization.

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we use the bond moment for Si–F of 2.3 *D* along with the observed dipole moments, then with tetrahedral bonding, $\mu_{\mathrm{SiH}} = 1.0$ or 3.6 *D*. However, the higher value of 3.6 *D* appears quite unreasonably large for a slightly polar bond with only a moderate $\overset{\longrightarrow}{\overset{-\ +}{\text{H-Si}}}$ homopolar moment supplementing the very small $\overset{\longrightarrow}{\overset{-\ +}{\text{H-Si}}}$ ionic moment. Therefore, it may be reasonably concluded that Si–H has a bond moment around 1.0 *D*. Such a conclusion is dependent, as is generally so, on the assumptions of bond additivity and the fairly close association of infrared bond moments with observed dipole moments.

Since methylsilane has a dipole moment[3] of 0.73 *D* and the butylsilanes and triethylsilane have dipole moments of 0.75–0.85 *D*, then with tetrahedral bonding, the Si–R bond has a moment of either 0.2 *D* or 1.8 *D* with the direction $\overset{\longrightarrow}{\overset{-\ +}{\text{R-Si}}}$.

The R–Si bond moment is made up of the Si–C bond moment and the C(sp³)–H bond moments. From infrared absorption and dispersion measurements,[22–25] the bond moments of $\mathrm{C(sp^3){-}H}$, $\mathrm{C(sp^2){-}H}$ and C(sp)–H obtained are ±0.31, ±0.63 and ±1.05, respectively. The C(sp)–H bond moment direction probably is $\overset{\longrightarrow}{\overset{-\ +}{\text{C-H}}}$.[25] The $\mathrm{C(sp^2){-}H}$ bond moment would also appear to have the direction $\overset{\longrightarrow}{\overset{-\ +}{\text{C-H}}}$.[24] The C–H bond in substituted benzenes has been found to be $\overset{\longrightarrow}{\overset{-\ +}{\text{C-H}}}$.[26,27] Recently Barrow and McKean[28] have determined the infrared absorption intensities in the methyl halides and concluded that in these compounds, the $\mathrm{C(sp^3){-}H}$ bond moment has the direction $\overset{\longrightarrow}{\overset{-\ +}{\text{C-H}}}$ with a magnitude around 0.4 *D*.[29] The experimental evidence thus favors a small $\mathrm{C(sp^3){-}H}$ bond moment of about 0.4 *D* with the hydrogen positive.[30]

If we use a $\overset{\longrightarrow}{\overset{-\ +}{\text{C-H}}}$ bond moment of 0.4 *D*, with a $\overset{\longrightarrow}{\overset{-\ +}{\text{R-Si}}}$ bond moment of 0.2 or 1.8 *D*, the $\overset{\longrightarrow}{\overset{-\ +}{\text{C-Si}}}$ bond moment would be either 0.6 or 2.2 *D*. The latter value seems excessively large for the C–Si bond moment considering the electronegativity difference of only 0.7 and the radius difference of only 0.83 Å. (proportional to the homopolar moment). Thus a $\overset{\longrightarrow}{\overset{-\ +}{\text{C-Si}}}$ bond moment of 0.6 *D* and a $\overset{\longrightarrow}{\overset{-\ +}{\text{R-Si}}}$ bond moment of 0.2 *D* seem reasonable.

On the basis of the foregoing discussion, the following bond moment magnitudes and directions may be assigned: $\overset{\longrightarrow}{\overset{-\ +}{\text{H-Si}}} = 1.0\ D$, $\overset{\longrightarrow}{\overset{-\ +}{\text{R-Si}}} = 0.2\ D$, $\overset{\longrightarrow}{\overset{-\qquad +}{\mathrm{C(sp^3){-}H}}} = 0.4\ D$ and $\overset{\longrightarrow}{\overset{-\ +}{\text{C-Si}}} = 0.6\ D$.

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[28] G. M. Barrow and D. C. McKean, *Proc. Roy. Soc.* (*London*), **A213**, 27 (1952).

[29] It is also of interest to note that if the bond moments of the C–H bonds with sp³, sp² and sp hybridization are assumed to be of the same sign and if these bond moments are plotted against their bond order, a straight line relationship results. See also ref. 25.

[30] Coulson, ref. 18, calculated theoretically a C–H bond moment of 0.3 *D* with the hydrogen *negative*. At the present time, the experimental evidence given above does not support this conclusion. Bell, *et al.*, ref. 26, argue that Coulson's results for a rigid molecule cannot be closely related to the bond moments obtained from bending vibrational modes in infrared intensity studies.

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[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

On the Separation of Inductive and Mesomeric Effects by Molecular Orbital Theory[1]

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Calculations of electron densities and localization energies by perturbation theory applied to the semi-empirical LCAO molecular orbital method are analyzed into four separate steps. The individual steps are used to separate the various effects used by the English school in the qualitative interpretation of the reactivity of conjugated organic compounds.

Theoretical treatments of the reactivity of conjugated and aromatic organic compounds by molecular orbital (MO) theory have been performed by use of two fundamentally different semi-empirical approaches—the electron density (static), and the localization methods.[2] It appeared of interest to examine whether an analysis of such calculations would permit a quantitative separation of the various effects which have been introduced in the qualitative interpretation of reactivity.[3] The crude calculations by the LCAO method, neglecting overlap integrals, are best suited for such an analysis, and in particular the perturbation treatment introduced by Coulson and Longuet-Higgins[4]

[1] Theoretical Considerations Concerning the Hammett Equation. VII. For the previous paper in this series see H. H. Jaffé, THIS JOURNAL, **76**, 5843 (1954).

[1a] Department of Chemistry, Univ. of Cincinnati, Cincinnati, Ohio.

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