

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Physical Properties of Organosilicon Compounds. II. Trimethylsilanol and Triethylsilanol

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Some of the physical properties of trimethylsilanol and triethylsilanol have been measured and compared to the properties of the corresponding alcohols, *i.e.*, *t*-butyl alcohol and 3-ethylpentanol-3. The silanols were found to be strongly associated in the liquid phase and in dilute cyclohexane solution. The physical properties of the silanols indicate a marked similarity between silanols and their carbon analogs. The enthalpies of vaporization, the entropies of vaporization and the dipole moments of the silanols are reported.

Introduction

Many well known classes of carbon compounds are represented by analogs in organosilicon chemistry in which one or more atoms of carbon have been replaced by silicon.¹ This is well exemplified by the existence of silanols, >SiOH -containing molecules, of which many examples have been reported.² Although formally similar to the alcohols of carbon chemistry, silanols are relatively unstable toward intermolecular condensation (to form siloxanes and water) and for this reason very few measurements of their physical properties have been carried out. In the present paper, the physical properties of trimethylsilanol and triethylsilanol are compared with those of the corresponding alcohols.

Experimental

Materials.—Trimethylsilanol was prepared by the hydrolysis of trimethylfluorosilane according to the method of Sommer, Pietrusza and Whitmore.³ This material boiled at 98.9° at one atmosphere and the refractive index of the sample was 1.3889 at 20° (lit. values, b.p. 99° (734 mm.);³ n_{20}^D 1.3888,³ n_{20}^D 1.3880.⁴

Triethylsilanol was prepared by the hydrolysis of triethylfluorosilane⁵; b.p. 63° (12 mm.), n_{20}^D 1.4329 (previous value, n_{20}^D 1.4329.³

Eastman Kodak Company 3-ethylpentanol-3 (triethylcarbinol) was dried over anhydrous potassium carbonate and distilled; b.p. 35° (5 mm.), n_{20}^D 1.4330, d_{20}^4 0.842 (previous values, b.p. $72\text{--}73^\circ$ (52 mm.),⁵ n_{20}^D 1.4266⁶ and n_{20}^D 1.4294,⁵ d_{20}^4 0.8407⁶; MR_D (obsd.) 35.81, MR_D (calcd.) 36.36.

Cyclohexane (E. I. du Pont de Nemours Co., Inc., Hytrol A) was dried over calcium hydride⁷ and distilled; b.p. 81.8° , n_{20}^D 1.4262 (previous values, b.p. 82° ,⁸ n_{20}^D 1.4262).⁹

Vapor Pressures.—Before the measurements of vapor pressure of the silanols were carried out, it was observed that dissolved air was removed from these materials with difficulty by standard out-gassing procedures. In order to eliminate this trouble, a sample of the silanol of approximately ten times the required volume was placed in a bulb on a vacuum chain over anhydrous sodium sulfate. After a thorough out-gassing operation, the silanol was allowed to stand in contact with the neutral drying agent overnight in

the absence of air and did not condense.¹⁰ About two-thirds of the original volume of silanol was then vacuum distilled into another bulb on the system. Approximately one-half of the distilled silanol was then pumped away. It was experimentally observed that the remaining portion of the silanol contained a minimum amount of dissolved air and that the material was suitable for the measurements of vapor pressure. These redistilled samples were introduced into the isoteniscope^{11,12} to be employed in the measurement of vapor pressure. The apparatus and method of measurement has been described previously.¹³

The vapor pressures of trimethylsilanol are presented in Table I.

TABLE I
VAPOR PRESSURE OF TRIMETHYLSILANOL

$t, ^\circ\text{C.}$	Obsd.	P_{mm} Calcd.	$t, ^\circ\text{C.}$	Obsd.	P_{mm} Calcd.
18.0	13.9	14.2	46.6	77.0	76.5
22.9	19.3	19.4	54.1	115.4	113.5
24.5	21.2	21.4	61.1	161.8	161.2
24.6	21.4	21.6	64.5	193.9	190.0
29.7	29.5	29.5	68.9	234.4	234.0
32.7	34.9	35.1	76.4	329.2	330.4
37.7	47.0	47.0	79.1	374.9	373.0
41.6	59.3	58.2	84.7	468.0	477.3

By application of the method of least squares to the data, the constants of equation 1 were evaluated.

$$\log_{10} P_{\text{mm}} = 9.3331 - \frac{2308.8}{T} \quad (1)$$

From the constants of equation 1, the enthalpy of vaporization of trimethylsilanol is found to be 10.9 ± 0.1 kcal./mole. The entropy of vaporization at normal boiling point (Trouton constant) is 29.4 e.u.

The extrapolated boiling point was found to be 97° . It will be observed that this value is lower than the literature value of 100° .⁴ However, it should be pointed out that trimethylsilanol tends to condense to hexamethyldisiloxane (with the splitting-out of water) at elevated temperatures. As a result, in the distillation of trimethylsilanol at atmospheric pressure, one usually attempts to flash over the product in order to avoid the condensation reaction. Therefore, the boiling points which have been previously reported may be somewhat in error.

(10) The stability of trimethylsilanol over anhydrous sodium sulfate was confirmed by a separate experiment in which no change of refractive index of the compound took place in 64 hours.

(11) A. Smith and A. W. C. Menzies, *THIS JOURNAL*, **32**, 1412 (1910).

(12) H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

(13) R. C. Osthoff, W. T. Grubb and C. A. Burkhard, *ibid.*, **75**, 2227 (1953).

(1) E. G. Rochow, "The Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 171, *et seq.*

(2) C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 97 (1947).

(3) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *THIS JOURNAL*, **68**, 2282 (1946).

(4) R. O. Sauer, *ibid.*, **66**, 1707 (1944).

(5) F. C. Whitmore and E. D. Badertscher, *ibid.*, **55**, 1559 (1933).

(6) J. Boeseken and S. J. Wildshut, *Rec. trav. chim.*, **51**, 168 (1932).

(7) D. T. Hurd, "An Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 44.

(8) J. C. Gjaldbaek and J. H. Hildebrand, *THIS JOURNAL*, **71**, 3147 (1949).

(9) A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **56**, 129 (1946).

The vapor pressure data for triethylsilanol which were observed by the authors are presented in Table II.

TABLE II
VAPOR PRESSURE OF TRIETHYLSILANOL

$t, ^\circ\text{C.}$	Obsd. P_{mm}	Calcd.	$t, ^\circ\text{C.}$	Obsd. P_{mm}	Calcd.
24.5	1.8	1.5	93.6	73.7	71.1
41.0	4.6	4.4	100.5	99.0	97.0
48.2	6.5	6.8	104.9	122.2	116.6
55.2	9.2	10.2	116.0	189.0	184.8
60.8	12.4	13.9	120.5	218.5	220.4
67.9	19.1	20.4	135.2	390.4	388.2
74.4	28.3	28.5	140.2	471.2	463.1
84.6	48.0	47.0			

A nearly linear relationship exists between the logarithm of the vapor pressure and the reciprocal of the absolute temperature. Equation 2 was determined by the method of least squares from the data of Table II.

$$\log_{10} P_{\text{mm}} = 9.0552 - \frac{2642.5}{T} \quad (2)$$

Solving equation 2 at $P_{\text{mm}} = 760$, gives a boiling point of 155° for triethylsilanol (previous value 153.5°). From equation 2, the enthalpy vaporization of triethylsilanol is found to be 12.1 ± 0.1 kcal./mole. The entropy of vaporization at the boiling point is 28.3 e.u.

In a manner similar to that described above, it was observed that the vapor pressure of 3-ethylpentanol-3 could be represented by equation 3

$$\log_{10} P_{\text{mm}} = 9.4407 - \frac{2678.1}{T} \quad (3)$$

From this equation, the enthalpy of vaporization is calculated to be 12.3 ± 0.2 kcal./mole and the entropy of vaporization at the boiling point is 29.7 e.u.

In Table III are presented the enthalpies and entropies of vaporization of trimethylsilanol, triethylsilanol and their carbon analogs.

TABLE III
COMPARISON OF ENTHALPIES AND ENTROPIES OF VAPORIZATION OF SILANOLS AND CARBINOLS

	ΔH_v	ΔS_v
$(\text{CH}_3)_3\text{SiOH}$	10.9	29.4
$(\text{CH}_3)_3\text{COH}$	9.7 ¹⁴	27.2 ¹⁴
$(\text{CH}_3\text{CH}_2)_3\text{SiOH}$	12.1	28.3
$(\text{CH}_3\text{CH}_2)_3\text{COH}$	12.3	29.7

Since the comparison of the entropies of vaporization, ΔS_v , listed in Table III indicate that these silanols and carbinols are associated in the liquid state to about the same extent, it was of interest to investigate the degree of association by measuring the molecular weights of these compounds in dilute solution.

Cryoscopic Measurements of Molecular Weight.—In several published papers molecular weights of siloxanes have been determined by means of cryoscopic measurements in cyclohexane.¹⁵⁻¹⁸ Although no data on the cryoscopic

(14) J. C. Brown, *J. Chem. Soc.*, **83**, 987 (1903).

(15) D. W. Scott, *THIS JOURNAL*, **68**, 357 (1946).

(16) M. J. Newing, *Trans. Faraday Soc.*, **46**, 613 (1950).

(17) C. A. Burkhard, *THIS JOURNAL*, **67**, 2173 (1945).

(18) M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

behavior of silanols have been reported, Sauer and Gilliam¹⁹ have shown that trimethylchlorosilane exhibits an association number of two in dilute cyclohexane solution indicating the possibility of an unusual association of the type found in aluminum chloride.²⁰ It is worthy of note that silanols could associate through $\rightarrow\text{SiO} \rightarrow \text{Si} \leftarrow$ similar to aluminum chloride or through hydrogen bonding.



The cryoscopic measurements were carried out in a small dewar flask (20 X 150 mm.) into which a Beckmann thermometer could be placed. The thermometer was held in place by means of a Teflon stopper which fit snugly into the top of the dewar flask. A stainless steel ring which fit around the thermometer was fastened to a wolfram rod. The rod was attached to an eccentric (electric motor driven) and thus the ring provided stirring. In operation, 25 cm.³ of the solution was placed in the dewar cell and the stirring commenced. At this point the cell was surrounded by ice and the temperature measured every half-minute. In this manner the cooling curves were obtained.

Preliminary experiments using benzene as the cryoscopic solvent indicated that trimethylsilanol was not appreciably associated in this medium ($M(\text{obsd.})$ 99.7, $M(\text{calcd.})$ 90.2) in the concentration range 0.033 to 0.149 molal. Two typical siloxanes, hexamethyldisiloxane and octamethylcyclotetrasiloxane, were not associated in benzene in a corresponding concentration range. However, in cyclohexane solution trimethylsilanol and triethylsilanol are associated to an extent which depends upon their concentration. Therefore, it was of interest to compare the cryoscopic molecular weights of the two silanols with those of the corresponding carbinol, *t*-butyl alcohol and 3-ethylpentanol-3.

In Table IV are presented the cryoscopic molecular weight at various concentration of trimethylsilanol, triethylsilanol and 3-ethylpentanol-3 as determined by the authors. The data of Dunkel²¹ for *t*-butyl alcohol in cyclohexane are also included. In Table IV, m is the molality and $M(\text{obsd.})$ is the apparent molecular weight, and $M(\text{obsd.})/M(\text{calcd.})$ is the association number.

TABLE IV APPARENT MOLECULAR WEIGHTS IN CYCLOHEXANE ^a					
$(\text{CH}_3)_3\text{SiOH}$, $M(\text{calcd.}) = 90.2$			$(\text{CH}_3)_3\text{COH}$, $M(\text{calcd.}) = 74.12$		
m	M (obsd.)	$M(\text{obsd.})$ $M(\text{calcd.})$	m	M (obsd.)	$M(\text{obsd.})$ $M(\text{calcd.})$
0.0151	160	1.78	0.0014	89	1.20
.0292	186	2.06	.0084	163	2.20
.0583	221	2.45	.0181	204	2.75
.1005	272	3.02	.0354	237	3.20
.1450	295	3.28	.066	256	3.46
			.255	296	3.98
			.386	300	4.05
$(\text{CH}_3\text{CH}_2)_3\text{SiOH}$, $M(\text{calcd.}) = 132.2$			$(\text{CH}_3\text{CH}_2)_3\text{COH}$, $M(\text{calcd.}) = 116.2$		
0.016	144	1.09	0.0241	132	1.14
.032	168	1.27	.0519	137	1.18
.072	207	1.57	.0997	146	1.26
.111	238	1.80	.140	152	1.31
.249	310	2.34	.213	166	1.43

^a The cryoscopic constant of the solvent was found to be 20.0 employing triphenylmethane as a solute.

It is to be observed that in the case of *t*-butyl alcohol, the association number tends to level off at four, indicating some sort of association to a tetrameric unit. Trimethylsilanol tends to ap-

(19) R. O. Sauer and W. F. Gilliam, *ibid.*, **66**, 1793 (1944).

(20) K. J. Palmer and N. Elliott, *ibid.*, **60**, 1852 (1938).

(21) H. Dunkel, *Z. Physik. Chem.*, **B45**, 201 (1939).

proach a limiting association number somewhere between three and four. This again is indicative of the similarity of these two liquids. On the other hand, triethylsilanol is definitely less associated than either trimethylsilanol or *t*-butyl alcohol, while 3-ethylpentanol-3 exhibits essentially no association. This result is not entirely unexpected since one would anticipate that the more highly hindered ethyl derivatives should be less associated than their methyl analogs.

Dipole Moments.—The dipole moments of trimethylsilanol, triethylsilanol, and 3-ethylpentanol-3 were evaluated from the dielectric properties of the pure liquids.²² The experimental data are summarized in Table V in which V is the molar

TABLE V
DIELECTRIC PROPERTIES

	V	$\tan \delta$	ϵ	μ
(CH ₃) ₃ SiOH	111.2	<0.0002	7.17 ± 0.03	2.01 ± 0.10
(CH ₃ CH ₂) ₃ SiOH	152.9	.0004	2.66 ± .02	0.62 ± .08
(CH ₃ CH ₂) ₃ COH	138.0	.002	3.24 ± .02	1.13 ± .05

(22) L. Onsager, *THIS JOURNAL*, **58**, 1490 (1936).

volume of the liquid at 20°, $\tan \delta$ is the loss factor, ϵ is the dielectric constant at 20° and 1000 cycles and μ is the dipole moment in Debye units.

The dipole moment *t*-butyl alcohol has been reported to be 1.74 D (Onsager moment).²³ The dipole moments vary considerably from the values which would be predicted for the unassociated liquids. This result is to be expected on the basis of the data obtained in careful studies of the dielectric properties of alcohols.^{24,25} Such behavior may be attributed to strong forces of association in the liquid state, as indicated by the high values of the entropies of vaporization and the high degree of association in cyclohexane solution.

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Diffusion of Benzene and Methylene Chloride Vapors into Polystyrene^{1,2}

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The rates of sorption and desorption of vapors of benzene and methylene chloride in films of polystyrene have been studied at 30 and 40° and at a variety of pressures. With low concentrations of either vapor the diffusion is anomalous in that the diffusion does not obey Fick's law with the usual assumption of equilibrium concentration of penetrant at the film surface. By studying sorption and desorption of benzene over narrow concentration intervals it is found that there is a critical concentration of benzene in the polymer above which diffusion is Fickian and below which it is anomalous. At both 30 and 40° the observed critical concentration for change in character of diffusion agrees closely with the critical concentration found by Fox for the second-order transition of polystyrene-solvent mixtures. In the region of anomalous diffusion, *i.e.*, below the second-order transition, the diffusion of either benzene or methylene chloride causes macromolecular orientation in the direction of diffusion and this orientation influences the rate of sorption.

Several recent studies³⁻⁷ of the diffusion of small molecule species into polymer films have shown that in some cases Fick's law

$$\frac{dc}{dt} = \frac{d}{dx} \left[D(c) \frac{dc}{dx} \right] \quad (1)$$

with the usually assumed boundary conditions, $C = C_{eq}$ at $x = 0$ and $x = l$ for all t , is obeyed whereas in other cases it is not. (In the above C is concentration of small molecule in the polymer in grams per gram, l is film thickness, x is distance in the film, t is time and $D(c)$ is the diffusion coefficient. C_{eq} is equilibrium concentration for the particular pressure of vapor under study.) A particularly interesting result obtained with acetone-polyvinylacetate is that with this system diffusion is normal above the second-order transition temperature for the polymer-solvent mixture

whereas below this temperature the diffusion is anomalous, *i.e.*, Fick's law with the above boundary conditions is not obeyed.⁸

To distinguish between normal and anomalous diffusion two criteria have been used. One is that for the initial diffusion into a polymer film, *i.e.*, until concentration at the film center changes appreciably, a plot of weight of vapor takeup or loss, Q , versus \sqrt{t} for either sorption or desorption should be linear if diffusion follows Fick's law with the above boundary conditions. A second criterion is that a plot of Q versus time for vapor sorption should show no inflections.

A suggestion that the influence of second-order transition on diffusion may be general is found in the facts that the diffusion at 25 to 45° of hydrocarbons into polyisobutylene ($T_g = -70^\circ$) is normal⁶ whereas diffusion at 30° of vapors into cellulose acetate⁵ and nitrate⁷ is highly anomalous and with these cellulose derivatives the second-order transition presumably occurs at temperatures above 100°. In order to obtain further evidence on this point we have studied the diffusion of two vapors,

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(2) Presented in part at 122nd Meeting of American Chemical Society, Atlantic City, N. J., September, 1952.

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