[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Organosilicon Fluoroesters

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RECEIVED JUNE 26, 1958

Table I lists the boiling points, densities, refractive indices and molar refractions of 20 new organosilicon heptafluoro-*n*-butyrates, pentafluoropropionates, trifluoroacetates, difluoroacetates and acetates. The average error in calculated molar refractions is 0.40% and the C–F bond refraction is close to 1.850. An empirical equation b.p. of ester = $n(0.250)$(b.p. of R_4Si) + $(4 - n)(k)$(b.p. of acid)—n is the number of alkyl groups attached to silicon, and temperatures are in °K.—fits the normal boiling point of 11 alkylsilicon fluoroesters with an average error of 6° for ethyl, *n*-propyl and *n*-amyl derivatives using 0.302 as k; the average error is 3° for phenylsilicon esters using 0.284 as k. Several other methods of calculating boiling points are unsatisfactory. Nine calculated Trouton constants of 26–33, average 29.5, suggest association in organosilicon esters due to the Si–O bond. These colorless esters all hydrolyze easily, generally have irritating odors, and tend to decompose at the normal boiling points.

Introduction

Authors of the many papers on organosilicon esters, known for approximately 100 years, report numerous difficulties, such as long times in preparations using sodium acetate, or low yields or the decomposition of the esters.[1–3] They usually report boiling points under reduced pressure only, and thus there is little opportunity for comparison of normal boiling points.

Organic fluorine compounds are now easily available and of much industrial importance. In the fluorocarbons there is much stability and the compounds have surprisingly low boiling points, such as 82.51° for *n*-C_7F_{16}, while *n*-C_7H_{16} boils at 98.43°.[4] Gradual introduction of fluorine into acetic acid causes increase in acid strength as the fluorine content increases and produces the lowest boiling point in *strong* trifluoroacetic acid: CH_3COOH, b.p. 118.1°; highly-toxic CH_2FCOOH, b.p. 165°; CHF_2COOH, b.p. 134.2°; CF_3COOH, b.p. 72.4°.

There is a method of boiling point numbers for calculating the boiling points of organosilicon chlorides and bromides but not fluorides, iodides or esters.[5]

Known organogermanium esters, closely related to organosilicon esters, include $(C_2H_5)_3GeOCOCF_3$, $(C_2H_5)_3GeOCOC_2F_5$ and $(C_2H_5)_3GeOCO$-*n*-C_3F_7, among many others.[6]

Both the stability of the fluorocarbons and the stability of the triethylgermanium fluoroesters suggest the desirability of isolation and study of a series of organosilicon fluoroesters, such as that in the present paper.

Experimental Results

Table I lists the boiling points, densities, refractive indices and molar refractions of 20 new organosilicon esters, 16 of which contain fluorine. Visible decomposition of 11 compounds at the normal boiling points limits the accuracy of the individual b.p. to ±1° or occasionally ±2°. These colorless compounds all hydrolyze quite easily and generally have irritating odors. Supercooled liquid $C_6H_5Si(OCOCH_3)_3$, although fairly viscous, easily allows determination of the density and refractive index as a liquid at 20°; cyclo-$C_6H_{11}Si(OCOC_2F_5)_3$ supercools very little.

Experimental

Starting materials included specially prepared silver salts of the four fluoroacids, also *n*-$C_5H_{11}SiCl_3$ made from *n*-$C_5H_{11}MgCl$ and $SiCl_4$; they included CH_3SiCl_3, $C_2H_5SiCl_3$, *n*-$C_3H_7SiCl_3$, cyclo-$C_6H_{11}SiCl_3$ and $C_6H_5SiCl_3$ from Dow Corning Corp., Midland, Mich. Equipment included apparatus with interchangeable ground joints, also pycnometers, transfer pipets and a micropipet for the usual measuring of the liquid and later titrating the available acidity—phenol red was the indicator for the phenylsilicon esters of perfluoroacids.

Typically, reflux of 18 mmoles of $RSiCl_3$ and 70 mmoles of $AgOCOR'$ for 70 minutes in 18–20 ml. of CCl_4 was followed by filtration and washing of silver salts, next by distillation of CCl_4 and then by fractional distillation of the organosilicon ester, rejecting the lowest-boiling 25%, taking the next 45% for study and leaving 30% undistilled. An average 12.6 mmoles of organosilicon ester was a yield of 70% and contained a trace of chlorine if any. Because of the easy hydrolysis, all the measurements of boiling point, density and refractive index required rapid manipulation in a room where the partial pressure of water vapor did not exceed 10 mm. Often a soda-lime absorber was necessary to prevent an easily volatile lachrymatory impurity, probably an acid anhydride, from entering the air in the room.

Analysis for silicon consisted of treatment of the compound with a mixture of fuming nitric and fuming sulfuric acids in a covered Vycor crucible, with final ignition to SiO_2. Analysis for available acidity included two closely agreeing determinations the average of which is in Table I.

Discussion

General Trends.—In an organosilicon ester of a perfluoroacid a *high* fluorine content is associated with a comparatively *high* liquid density, *low* refractive index and *low* normal boiling point. Although the density of *n*-$C_3H_7Si(OCOCHF_2)_3$ at 20° appears to be out of line, there is a proper fit in the density at the normal boiling point, thus at a comparable state. Use of the expansion coefficient 0.00120 obtained with *n*-$C_3H_7Si(OCOC_2F_5)_3$ and a dilatometer gives these values for the three esters at the b.p. of each: *n*-$C_3H_7Si(OCOCH_3)_3$, density 0.809 and molar volume 308 ml., *n*-$C_3H_7Si(OCOCHF_2)_3$, density 1.076 and molar volume 332 ml. (calculated 331 ml. from the other two values); *n*-$C_3H_7Si(OCOCF_3)_3$, density 1.198 and molar volume 342 ml. The same correction should apply to $C_6H_5Si(OCOCHF_2)_3$. When compared with the corresponding esters the acetates have relatively *high* boiling points and refractive indices and *low* densities.

Molar Refractions.—Some explanation is necessary for the molar refractions calculated in Table I. Vogel and co-authors list or furnish data that give these satisfactory values for bond refractions used in the calculations in Table I: C–C, 1.296; C–H, 1.676; O—C=O in esters, 4.98; Si–C, 2.52; Si–O, 1.80; also C_6H_5–Si, 27.61.[7] How-

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(4) G. D. Oliver and others, *ibid.*, **73**, 5722 (1951).

(5) R. N. Lewis and A. E. Newkirk, *ibid.*, **69**, 701 (1947).

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(7) A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954); A. I.

TABLE I

PROPERTIES OF NEW ORGANOSILICON FLUOROESTERS

Compound	B.p., Found	°C. Calcd.	d^{20}_4	n^{20}[a]	Mol. refr. Calcd.	Mol. refr. Found	OCOR[b] Calcd.	OCOR[b] Found	Silicon[c] Calcd.	Silicon[c] Found	Distilled °C.	at— Mm.
n-$C_3H_7Si(OCOCH_3)_3$	237	...	1.119	1.4160	56.16	55.69	71.3	71.1	11.3	11.0	121–122	12
n-$C_3H_7Si(OCOCHF_2)_3$	230[d]	217.6	1.440	1.3771	57.20	56.91	80.0	80.2	7.9	7.8	130–132	12
n-$C_3H_7Si(OCOCF_3)_3$	157	161.7	1.434	1.3277	57.72	57.99	82.7	82.5	6.8	6.6	82–83	42
n-$C_3H_7Si(OCOC_2F_5)_3$	178[d]	183.9	1.510	1.3156	72.71	72.69	87.3	87.6	5.0	4.9	99–100	41
n-$C_3H_7Si(OCOC_3F_7)_3$	208[d]	205.7	1.584	1.3164	87.70	88.04	90.0	90.5	4.0	3.8	123–125	33
$C_6H_{11}Si(OCOCH_3)_3$	275[d]	...	1.134	1.4442	68.04	67.59	61.4	61.5	9.7	9.8	126–128	1
$C_6H_{11}Si(OCOCF_3)_3$	200	...	1.418	1.3583	69.61	69.79	75.3	75.4	6.2	6.2	96–98	11
$C_6H_{11}Si(OCOC_2F_5)_3$[e]	216	...	...	....	...	...	81.5	82.0	4.7	4.7	111–112	14
$C_6H_{11}Si(OCOC_3F_7)_3$	243[d]	...	1.566	1.3370	99.59	99.63	85.2	84.9	3.7	3.4	128–129	11
$C_6H_5Si(OCOCH_3)_3$[f]	268[d]	...	1.200	1.4775	66.92	66.54	62.7	62.8	10.0	9.7	143–145	1
$C_6H_5Si(OCOCHF_2)_3$	248[d]	249.1	1.494	1.4290	67.96	67.34	73.0	72.9	7.2	7.2	132–134	1
$C_6H_5Si(OCOCF_3)_3$	198	196.5	1.481	1.3784	68.48	69.22	76.3	76.6	6.3	6.3	95–96	14
$C_6H_5Si(OCOC_2F_5)_3$	215	217.4	1.546	1.3551	83.47	83.80	82.3	81.9	4.7	4.8	106–107	11
$C_6H_5Si(OCOC_3F_7)_3$	245[d]	237.9	1.617	1.3495	98.46	98.91	85.9	85.7	3.8	3.6	128–130	12
n-$C_5H_{11}Si(OCOCH_3)_3$	255[d]	...	1.074	1.4218	65.46	65.37	64.1	63.9	10.2	10.2	122–123	2
n-$C_5H_{11}Si(OCOCF_3)_3$	181[d]	187.6	1.363	1.3410	67.02	67.59	77.4	77.6	6.4	6.2	96–97	20
n-$C_5H_{11}Si(OCOC_2F_5)_3$	197[d]	209.9	1.441	1.3267	82.01	82.53	83.2	83.6	4.8	4.7	107–108	18
$C_2H_5Si(OCOC_2F_5)_3$	169	168.9	1.545	1.3091	68.06	67.95	89.6	90.1	5.1	5.1	100–101	55
$C_2H_5Si(OCOC_3F_7)_3$	199	190.7	1.624	1.3111	83.05	82.88	91.8	92.1	4.0	3.8	128–129	47
$CH_3Si(OCOC_2F_5)_3$	159	...	1.589	1.3033	63.51	63.26	91.9	92.0	5.3	5.0	87–88	42

[a] In white light. All compounds are colorless. [b] Average of two close values by titration. [c] Weighed as SiO_2. [d] Decomposition occurred during measurement of normal b.p. [e] Solid of m.p. 46°. [d] Measurements on supercooled liquid; m.p. of solid is 36.5°.

ever, a value of 1.44 for the C–F bond refraction is in considerable error and is unacceptable.[7] Suitable data on fluorocarbons without hydrogen makes available values of 1.845[8] and 1.855[9] averaging 1.850 as used herein.

Another method of obtaining the C–F bond refraction is subtraction of the *MR* of n-$C_3H_7Si(OCOCF_3)_3$ from the *MR* of n-$C_3H_7Si(OCO$-n-$C_3F_7)_3$, obtaining 30.05 for 3 CF_2–CF_2– groups, or 10.016 per group; then subtraction of 2.592 for the two C–C bond refractions and finally division by 4 gives 1.856 for the C–F bond refraction directly. Similarly, the corresponding cyclohexylsilicon esters furnish 1.839 and the phenylsilicon esters 1.826 for C–F. All three values indicate an average of 1.84 ± 0.01, confirming the value of 1.850 selected above.[8,9]

Boiling Points.—Two previous methods of calculating boiling points are unsuited for the organosilicon esters in Table I. A general method of boiling point numbers uses the equation

$$\text{B.p. (in °C.)} = 230.14 \sqrt[3]{\text{B.P.N.}} - 543$$

and is adequate for organic compounds,[10] also certain organosilicon compounds excluding those with Si–Si, Si–O and Si–F bonding.[5] Now, use of the appropriate boiling point numbers[5] for Si and for R in $RSi^{\equiv}$ (R is CH_3, C_2H_5, n-C_3H_7 or C_6H_5) and solving each equation yields the individual boiling point number for $OCOCF_3$ in four esters to be: 6.17 in $CH_3Si(OCOCF_3)_3$,[11] 5.37 in $C_2H_5Si(OCOCF_3)_3$,[12] 4.82 in n-$C_3H_7Si(OCOCF_3)_3$ and 3.44 in $C_6H_5Si(OCOCF_3)_3$. No average boiling point number can fit all four cases. Moreover, further calculations of boiling point numbers in organosilicon (iso)cyanates and isothiocyanates—with methyl, ethyl and phenyl as the organic groups[13,14] —shows that this method is inaccurate.

A special method of boiling point increments, such as for the change of Cl to NCO or Cl to NCS,[15] is of no value with organosilicon esters.

An empirical equation, herein supposedly used for the first time

$$\text{B.p. of ester} = (n)(0.250)(\text{b.p. of } R_4Si) + (4 - n)(k)(\text{b.p. of acid})$$

uses n for the number of alkyl groups attached to silicon and uses temperatures in °K. This equation fits the normal boiling points of 11 alkylsilicon fluoroesters with an average error of 6° using 0.302 as k for ethyl, n-propyl and n-amyl derivatives; the average error is 3° for 4 phenylsilicon esters using 0.284 as k. Table I lists the calculated b.p.s. of 8 alkylsilicon fluoroesters and all 4 phenylsilicon fluoroesters. In addition the empirical equation furnishes calculated b.p.'s of 151.3° (actual 153.0°) for $(C_2H_5)_3SiOCOCF_3$,[12] 149.0° (actual 155.0°) for $(C_2H_5)_2Si(OCOCF_3)_2$[16] and 146.6° (actual 148.5°) for $C_2H_5Si(OCOCF_3)_3$.[12] All calculations involve later change into °K. of the normal boiling points in °C.: CF_3COOH, 72.4; CHF_2COOH,

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(16) H. H. Anderson, *ibid.*, **74**, 2372 (1952).

134.2; C_2F_5COOH, 97.0; *n*-C_3F_7COOH, 121.0[17]; $(C_2H_5)_4Si$, 153.7; (*n*-$C_3H_7)_4Si$, 214; (*n*-$C_5H_{11})_4Si$, 318[18]; $(C_6H_5)_4Si$, 428.[5] No b.p. is available for $(C_6H_{11})_4Si$.

This empirical equation does not fit the normal boiling points of esters containing the CH_3–Si linkage; here the comparatively great difference in size between the CH_3 and the $OCOC_2F_5$ groups may be important. Kopp's data allow approximate calculation of the molar volumes of the alkyl and the ester groups at the b.p.s., as shown: CH_3, 27.5; C_2H_5, 49.5; *n*-C_3H_7, 71.5; *n*-C_5H_{11}, 115.5; $OCOCF_3$, 69.0; $OCOC_2F_5$, 97.4; OCO-*n*-C_3F_7, 125.8 ml. The *cyclic* C_6H_5, molar volume 93.5 ml., requires a reduction of *k* from 0.302 to 0.284 for the equation to fit the b.p.s.

In addition, this empirical equation does not appear to fit the boiling points of organosilicon acetates. Possible dipole–dipole interactions in the ester groups of the acetates might differ from those in the perfluoroesters; thus altered b.p.'s might result.

This type of empirical equation also fits the boiling points of numerous **alkylgermanium esters**—as has been known since April, 1953, and will be demonstrated in a future publication. Use of 0.370 for *k* in the empirical equation above furnishes satisfactory calculated normal b.p.s. of 182.6° (actual 183°) for $(C_2H_5)_3GeOCOCF_3$, 191.7° (actual 189.6°) for $(C_2H_5)_3GeOCOC_2F_5$, and 200.6° (actual 201.0°) for $(C_2H_5)_3$GeOCO-*n*-C_3F_7.[6]

Trouton's Constants.—The following are calculated Trouton constants—molar heat of vaporization divided by the normal boiling point in °K.—for nine esters: *n*-$C_3H_7Si(OCOCF_3)_3$, 27.4; *n*-$C_3H_7Si(OCOC_2F_5)_3$, 27.5; *n*-C_3H_7Si(OCO-*n*-$C_3F_7)_3$, 31.0; *n*-$C_3H_7Si(OCOCHF_2)_3$, 33.6; $C_2H_5Si(OCOC_2F_5)_3$, 26.1; C_2H_5Si(OCO-*n*-$C_3F_7)_3$, 31.4; *n*-$C_5H_{11}Si(OCOCF_3)_3$, 31.6; $CH_3Si(OCOC_2F_5)_3$, 28.2; also, $C_6H_5Si(OCOCF_3)_3$, 28.5. An average of 29.5 is consistent with some molecular association, supposedly due to the nature of the Si–O bond.

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