Boiling Points of Organogermanium Carboxylates and Mercaptides

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Application of the empirical equation: b.p. of $R_nGe(OCOR')_{4-n} = n(0.250)$(b.p. of R_4Ge) + $(4 - n)(k)$(b.p. of R′COOH) furnishes adequate results (root mean square error, 6.3°; standard deviation, 6.6°) in calculations of normal boiling points of 46 organogermanium carboxylates. All temperatures are in ° K., while k is 0.3425 for $RGe(OCOR')_3$ and $R_2Ge(OCOR')_2$, 0.3767 for $(C_2H_5)_3GeOCOR'$, and 0.3527 for $(n\text{-}C_3H_7)_3GeOCOR'$, $(iso\text{-}C_3H_7)_3GeOCOR'$, and $(n\text{-}C_4H_9)_3GeOCOR'$. Application of the new related empirical equation: b.p. of R_3GeSR' = 0.750 (b.p. of R_4Ge) + 0.527 (b.p. of R′SH) furnishes satisfactory results (root mean square error, 6.3°; standard deviation, 6.6°) in calculations of normal boiling points of nine triethylgermanium mercaptides.

THE KINNEY EQUATION:

$$\text{B.P. in °C.} = 230.14\ (\text{total boiling point number})^{1/3} - 543 \quad (1)$$

gives adequate results in calculations of the normal boiling points of hydrocarbons (*5–7*), perfluoroalkanes, perfluorocycloalkanes, and perfluoroalkenes (*2*), and numerous substituted perfluoroalkanes (*2*), silanes and organosilicon compounds (*9*), boranes and alkylboron compounds (*2*), alkyl derivatives of bivalent sulfur, selenium, and tellurium (*2*), and organic derivatives of trivalent phosphorus (*2*) and arsenic (*2*). However, the equation is unsatisfactory for calculations of normal boiling points of organosilicon carboxylates (*4*).

An apparently new empirical equation:

$$\text{B.p. of ester} = (n)(0.250)(\text{b.p. of } R_4Si) + (4 - n)(k)(\text{b.p. of acid}) \quad (2)$$

uses n for the number of alkyl or aryl groups attached to silicon; all temperatures are in ° K. This equation fits the normal boiling points of 11 alkylsilicon fluoroesters with a simple average error of 5.7° using 0.302 for k, and fits 4 phenylsilicon fluoroesters with a simple average error of 3° using 0.284 for k (*4*). However, the equation fits neither acetates nor compounds with the CH_3—Si linkage.

Equation 2 upon slight alteration furnishes a new equation:

$$\text{B.p. of } R_nSi(OCOR')_{4-n} = n(0.250)(\text{b.p. of } R_4Si) + (4 - n)(k)(\text{b.p. of R'COOH}) \quad (3)$$

which now leads to two supposedly new empirical equations for calculations of normal boiling points of organogermanium carboxylates and mercaptides used in the present publication.

Application of the supposedly new empirical equation:

$$\text{B.p. of } R_nGe(OCOR')_{4-n} = n(0.250)(\text{b.p. of } R_4Ge) + (4 - n)(k)(\text{b.p. of R'COOH}) \quad (4)$$

now furnishes adequate results (simple average error, 5.0°; root mean square error, 6.3°; standard deviation, 6.6°) in calculations of normal boiling points of 46 organogermanium carboxylates; this involves temperatures in ° K. and suitable values for k. Appropriate values for k follow: 0.3425 for $RGe(OCOR')_3$ and $R_2Ge(OCOR')_2$; 0.3767 for $(C_2H_5)_3GeOCOR'$; 0.3527 for $(n\text{-}C_3H_7)_3GeOCOR'$, $(iso\text{-}C_3H_7)_3GeOCOR'$ and $(n\text{-}C_4H_9)_3GeOCOR'$. Here R is the alkyl group ethyl, n-propyl, isopropyl or n-butyl; n is the number of alkyl groups attached to germanium; R′ is an alkyl group or, with carboxylates only, a haloalkyl group. In Equation 4 or Equation 5 use the following normal boiling points in ° K.: $(C_2H_5)_4Ge$, 437.8; $(n\text{-}C_3H_7)_4Ge$, 498.6; $(n\text{-}C_4H_9)_4Ge$, 551.1 (*1*). Also use 498.6° K. for the normal boiling point of the yet unprepared and perhaps sterically hindered $(iso\text{-}C_3H_7)_4Ge$ (*1*); this estimate should involve an error of less than 5°. In 1949, personal measurements established the normal boiling point of $(C_2H_5)_4Ge$ as 437.8° K. or 164.7° C., further supported by an earlier (*8*) uncorrected boiling point of 163.5° C. A normal boiling point of 498.6° K. for $(n\text{-}C_3H_7)_4Ge$ used in Equation 4 represents the best value between the boiling point range 225–227° C. (*1*) and the earlier boiling point of 225° C. under 746 mm. pressure (*10*).

Application of the supposedly new related empirical equation:

$$\text{B.p. of } R_3GeSR' = 0.750\ (\text{b.p. of } R_4Ge) + 0.527\ (\text{b.p. of R'SH}) \quad (5)$$

now furnishes satisfactory results (simple average error, 4.7°; root mean square error, 6.3°; standard deviation, 6.6°) in calculations of normal boiling points of nine triethylgermanium mercaptides.

In Table I there are calculated normal boiling points (converted to ° C.) of 46 organogermanium carboxylates and of nine triethylgermanium mercaptides, with an overall simple average error of 5.0° and a root mean square error of 6.3°—the minimum for the 55 compounds through use of these empirical equations.

Table I. Calculations of Boiling Points

Compound	B.P., °C. Calcd.	Found	Error	Ref.
$C_2H_5Ge(OCOH)_3$[a]	220.3	230[d]	−9.7	(1)
$C_2H_5Ge(OCOCH_3)_3$	238.3	249	−10.7	(1)
$C_2H_5Ge(OCOC_2H_5)_3$	262.0	256	6.0	(1)
$C_2H_5Ge(OCO\text{-}n\text{-}C_3H_7)_3$	285.1	271[d]	14.1	(1)
$C_2H_5Ge(OCO\text{-}n\text{-}C_4H_9)_3$	309.1	305	4.1	(1)
$(C_2H_5)_2Ge(OCOH)_2$	201.8	210	−8.2	(1)
$(C_2H_5)_2Ge(OCOCH_3)_2$[a]	213.8	217	−3.2	(1)
$(n\text{-}C_3H_7)_2Ge(OCOCH_3)_2$	244.2	244.6	−0.4	(1)
$(n\text{-}C_3H_7)_2Ge(OCOCH_2Cl)_2$	292.8	296	−3.2	(1)
$(\text{iso-}C_3H_7)_2Ge(OCOCH_3)_2$	244.2	236	8.2	(1)
$(\text{iso-}C_3H_7)_2Ge(OCOC_2H_5)_2$	260.0	255	5.0	(1)
$(\text{iso-}C_3H_7)_2Ge(OCO\text{-}n\text{-}C_3H_7)_2$	275.4	274	1.4	(1)
$(\text{iso-}C_3H_7)_2Ge(OCOCH_2Cl)_2$	292.8	298	−5.2	(1)
$(C_2H_5)_3GeOCOH$[b]	196.1	185.7	10.4	(1)
$(C_2H_5)_3GeOCOCH_3$	202.6	190.5	12.1	(1)
$(C_2H_5)_3GeOCOCH_2Br$	236.5	244	−7.5	(3)
$(C_2H_5)_3GeOCOCH_2Cl$	229.4	234	−4.6	(3)
$(C_2H_5)_3GeOCOCHCl_2$	231.3	248	−16.7	(3)
$(C_2H_5)_3GeOCOCF_3$	185.5	183	2.5	(1)
$(C_2H_5)_3GeOCOC_2H_5$	211.3	205	6.3	(3)
$(C_2H_5)_3GeOCOCHClCH_3$	228.2	235	−6.8	(3)
$(C_2H_5)_3GeOCOCH_2CH_2Cl$	235.0	236	−1.0	(3)
$(C_2H_5)_3GeOCOC_2F_5$	194.5	189.6	4.9	(1)
$(C_2H_5)_3GeOCO\text{-}n\text{-}C_3H_7$	220.0	221	−1.0	(3)
$(C_2H_5)_3GeOCO\text{-}n\text{-}C_3F_7$	203.6	201.0	2.6	(1)
$(C_2H_5)_3GeOCO\text{-}n\text{-}C_4H_9$	228.6	230	−1.4	(3)
$(n\text{-}C_3H_7)_3GeOCOH$[c]	232.8	233	−0.2	(1)
$(n\text{-}C_3H_7)_3GeOCOCH_3$	239.0	236	3.0	(1)
$(n\text{-}C_3H_7)_3GeOCOCH_2Br$	270.7	267[d]	3.7	(1)
$(n\text{-}C_3H_7)_3GeOCOCH_2Cl$	264.0	265[d]	−1.0	(1)
$(n\text{-}C_3H_7)_3GeOCOCHCl_2$	265.7	266[d]	−0.3	(1)
$(n\text{-}C_3H_7)_3GeOCOCF_3$	222.8	226	−3.2	(1)
$(n\text{-}C_3H_7)_3GeOCOC_2H_5$	247.1	246	1.1	(1)
$(\text{iso-}C_3H_7)_3GeOCOCH_3$	239.0	229	10.0	(3)
$(\text{iso-}C_3H_7)_3GeOCOCH_2Br$	270.7	271[d]	−0.3	(3)
$(\text{iso-}C_3H_7)_3GeOCOCH_2Cl$	264.0	269	−5.0	(3)
$(\text{iso-}C_3H_7)_3GeOCOCHCl_2$	265.7	275	−9.3	(3)
$(\text{iso-}C_3H_7)_3GeOCOCF_3$	222.8	220	2.8	(3)
$(\text{iso-}C_3H_7)_3GeOCOC_2H_5$	247.1	242	5.1	(3)
$(\text{iso-}C_3H_7)_3GeOCOCHClCH_3$	262.8	269	−6.2	(3)
$(\text{iso-}C_3H_7)_3GeOCO\text{-}n\text{-}C_3H_7$	255.0	256	−1.0	(3)
$(\text{iso-}C_3H_7)_3GeOCO\text{-}n\text{-}C_4H_9$	263.3	266	−2.7	(3)
$(n\text{-}C_4H_9)_3GeOCOH$[c]	272.1	267	5.1	(1)
$(n\text{-}C_4H_9)_3GeOCOCH_3$	278.3	272	6.3	(1)
$(n\text{-}C_4H_9)_3GeOCOCF_3$	262.1	262	0.1	(1)
$(n\text{-}C_4H_9)_3GeOCO\text{-}n\text{-}C_6H_{13}$	315.5	324[d]	−8.5	(1)
$(C_2H_5)_3GeSC_6H_5$[e]	288.5	286	2.5	(3)
$(C_2H_5)_3Ge\text{-}o\text{-}SC_6H_4CH_3$	301.6	297.5	4.1	(3)
$(C_2H_5)_3Ge\text{-}m\text{-}SC_6H_4CH_3$	303.3	300	3.3	(3)
$(C_2H_5)_3GeSCH_2C_6H_5$	301.7	305	−3.3	(3)
$(C_2H_5)_3Ge\text{-}o\text{-}SC_6H_4NH_2$	322.5	326	−3.5	(3)
$(C_2H_5)_3GeS\text{-}n\text{-}C_6H_{13}$	277.9	277	0.9	(3)
$(C_2H_5)_3GeS\text{-}n\text{-}C_7H_{15}$	292.1	288	4.1	(3)
$(C_2H_5)_3GeSCH_2OC_4H_3$	280.9	276	4.9	(3)
$(C_2H_5)_3Ge\text{-}2\text{-}SC_{10}H_7$	351.0	367	−16.0	(3)

[a] Equation 4; *k* is 0.3425. [b] Equation 4; *k* is 0.3767. [c] Equation 4; *k* is 0.3527. [d] With decomposition. [e] Equation 5; *k* is 0.527. [f] A furfuryl mercaptide.

LIMITATION

Table I excludes dimethylgermanium diacetate (*1*), the only methylgermanium carboxylate and not comparable with any analogous compounds, and triethylgermanium thioacetate (*3*), which is neither a mercaptide nor a carboxylate.

DISCUSSION OF RESULTS

Calculations of the normal boiling points of 55 organogermanium carboxylates and triethylgermanium mercaptides via Equations 4 and 5, respectively, involve an over-all simple average error of 5.0°, root mean square error of 6.3°, and a standard deviation of 6.6°. Three different values for *k* serve in calculations on carboxylates, while a considerably higher fourth value of *k* serves in calculations on mercaptides. The considerably higher value of *k* in calculations of normal boiling points of triethylgermanium mercaptides appears related to the monomeric nature of mercaptans, while carboxylic acids have association through hydrogen bonding.

In calculations of normal boiling points—via Equations 4 and 5—the values of *k* (0.3425, 0.3527, and 0.3767) for the three series of organogermanium carboxylates are higher than the previous values of *k* (0.302 and 0.284) for the two series of organosilicon carboxylates (*4*).

Calculations of normal boiling points of four compounds of the $(\text{iso-}C_3H_7)_2Ge(OCOR')_2$ type and nine compounds of the $(\text{iso-}C_3H_7)_3GeOCOR'$ type involve an over-all simple average error of 4.8°. Thus the use of the same normal boiling point for both $(\text{iso-}C_3H_7)_4Ge$ and $(n\text{-}C_3H_7)_4Ge$ in Equation 4 appears mathematically adequate.

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