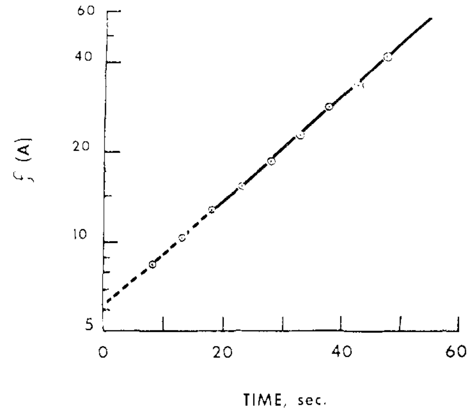

Fig. 4.—Plot for rate constant, k_1, for the dissociation of benzaldehyde–sodium bisulfite in water at 13°. Dotted line corresponds to extrapolated points; k_1 = slope/1.011.

Table I summarizes the values obtained for the equilibrium constant, the thermodynamic functions for the dissociation and the rate constants for dissociation and association. For comparison the values reported by Gubareva at 30° are listed.

TABLE I

T, (°C.)	13	23	33	30 (lit.)[1]
K (l./mole) $\times 10^5$	7.09	21.1	53.8	229
ΔH (kcal./mole)	17.7	17.7	17.7	7.20
ΔS (cal./mole deg.)	42.9	43.0	42.9	12.2
ΔF (kcal./mole)	5.43	4.98	4.58	3.68
k_1 (sec.$^{-1}$)	0.017	...	...	...
k_2 (l./mole sec.)	245	...	...	...

Gubareva also used iodimetric titrations to study the dissociation constants for the bisulfite complexes of a number of aliphatic aldehydes and ketones. He reported K's in the range of 10^{-3} to 10^{-5} and an average value of 7.9 kcal./mole for the ΔH's of dissociation. These values could likewise be subject to error arising from dissociation of the complex during the titration, as may be indicated by the fact that these ΔH's are only about half as large as the ΔH of dissociation found for the benzaldehyde bisulfite complex in this work. Gubareva's ΔH values would indicate that the bond strength of the bisulfite complex is no stronger than that of a strong hydrogen bond. Better values for the equilibrium constants of aliphatic carbonyl bisulfite complexes might be obtained by adding known amounts of the aliphatic carbonyl compound (or its bisulfite salt) to solutions of benzaldehyde sodium bisulfite and using ultraviolet spectra to determine the effect on the concentration of dissociated benzaldehyde. A straightforward, but somewhat cumbersome, relationship exists between the amount of benzaldehyde and the equilibrium constant of the aliphatic carbonyl bisulfite complex in such a system. Error from the absorbance of the aliphatic carbonyl compounds would be negligible since at 250 mμ the molar absorptivities of most of them are only about 0.1% of that of benzaldehyde. This Laboratory does not expect to carry out additional work along these lines.

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

n-Butylhalogermanes with Hydride Bonding[1]

BY HERBERT H. ANDERSON

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Gradually added deficiencies of $HgCl_2$, $HgBr_2$ or I_2 change previously known n-$C_4H_9GeH_3$ into the respective new compounds n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$ and n-$C_4H_9GeH_2I$, all of which have penetrating odors. Similarly, $HgCl_2$, $HgBr_2$ or I_2 change previously known $(n\text{-}C_4H_9)_2GeH_2$—for which there is now a b.p. of 173° under 760 mm.—into new $(n\text{-}C_4H_9)_2GeHCl$, $(n\text{-}C_4H_9)_2GeHBr$ and $(n\text{-}C_4H_9)_2GeHI$. These six new compounds appear to be the first examples of the $RGeH_2X$ or R_2GeHX types in which R is an alkyl group and X is a halogen. Aqueous ammonia and a solution of previously known n-$C_4H_9GeCl_3$ in CCl_4 furnish polymeric white solid $[(n\text{-}C_4H_9GeO)_2O]_n$, which reacts with hot concentrated HBr to give a partial yield of n-$C_4H_9GeBr_3$. Table I lists the properties and analyses of 8 new compounds and presents adequate data on n-$C_4H_9GeCl_3$.

Introduction

Six earlier publications establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to germanium[2a] in $(C_2H_5)_3GeH$, to tin[2b] in $(C_2H_5)_3SnH$ or to silicon in $(C_2H_5)_3SiH$,[3] $(C_2H_5)_2SiH_2$, n-$C_7H_{15}SiH_3$,[4] cyclo-$C_6H_{11}SiH_3$[5] or n-$C_4H_9SiH_3$.[6]

Gradual addition of $HgCl_2$, $HgBr_2$, AgNCO, AgNCS or I_2 to an excess of the appropriate alkylsilane or dialkylsilane allows relatively straightforward preparation of partially substituted compounds such as n-$C_7H_{15}SiH_2Cl$,[4] $(C_2H_5)_2SiHBr$,[3] cyclo-$C_6H_{11}SiH_2NCO$,[5] cyclo-$C_6H_{11}SiH_2NCS$[5] or n-$C_4H_9SiH_2I$.[6] Moreover, the careful treatment[6] of n-$C_4H_9SiH_3$, b.p. 56°, with $HgCl_2$, $HgBr_2$ or I_2 at either 10 or 22° to obtain n-$C_4H_9SiH_2Cl$, n-$C_4H_9SiH_2Br$ or n-$C_4H_9SiH_2I$, respectively, suggests methods for later preparation of the corresponding compounds n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$ and n-$C_4H_9GeH_2I$.

A recent publication lists the properties of n-$C_4H_9GeH_3$, $(n\text{-}C_4H_9)_2GeH_2$ and a number of other

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[1] Presented at the Third Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, February, 1960.

[2] (a) H. H. Anderson, THIS JOURNAL, **79**, 326 (1957); (b) **79**, 4913 (1957).

[3] H. H. Anderson, *ibid.*, **80**, 5083 (1958).

[4] H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

[5] H. H. Anderson, *ibid.*, **81**, 4785 (1959).

[6] H. H. Anderson, *ibid.*, **82**, 1323 (1960).

Table I

Properties of New *n*-Butylgermanium Compounds (Except Second)

Compound[a]	B.p.,[b] °C.	$d^{20}{}_4$	n^{20} [c]	Mol. refr. Calcd.	Mol. refr. Found	Germanium Calcd.	Germanium Found	Halogen Calcd.	Halogen Found	Distilled at °C.	Distilled at Mm.
n-$C_4H_9GeH_2Cl$	140.0	1.246	1.4598	36.80	36.74	43.4	43.1	21.2	21.2[d]	89–90	138
n-$C_4H_9GeCl_3$[e]	184	1.451	1.4750	44.82	45.81	30.8	30.5	45.1	45.1	83.5–84.0	24
n-$C_4H_9GeH_2Br$	159	1.536	1.4910	40.30	39.91	34.3	34.2	37.8	37.8	94–95	91
n-$C_4H_9GeBr_3$	237	2.132	1.5548	55.32	55.60	19.7	19.9	64.9	64.9	61–63	1
n-$C_4H_9GeH_2I$	181	1.776	1.5412	45.90	45.78	28.1	27.7	49.1	49.1	84.5–85.5	27
n-$C_4H_9GeI_3$	310[f]	2.647	....	79.08	...	14.2	14.0	74.6	74.7	119–121	1
$(n$-$C_4H_9)_2GeHCl$	219	1.107	1.4618	55.23	55.43	33.3	33.0	15.9	16.0	105.4–105.6	17
$(n$-$C_4H_9)_2GeHBr$	234	1.305	1.4832	58.73	58.62	27.1	27.1	29.9	29.9	112–113	14
$(n$-$C_4H_9)_2GeHI$	249	1.470	1.5148	64.33	64.54	23.1	22.9	40.3	40.4	73–75	1

[a] All compounds are colorless except the pale yellow n-$C_4H_9GeI_3$. [b] Under 760 mm. pressure. [c] In white light. [d] All analyses for halogen represent averages of two closely agreeing determinations. [e] Mentioned in ref. 7 without data. [f] With some decomposition.

closely related alkylgermanium hydrides. This paper[7] gives the Ge–H bond refraction as 3.59 and mentions the reaction of n-C_4H_9MgCl and $GeCl_4$ to give n-$C_4H_9GeCl_3$, for which there are no data.

This publication represents, in turn and apparently for the first time, organogermanium compounds containing a halogen, Ge–H and one or two alkyl groups in the same molecule: n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$, n-$C_4H_9GeH_2I$, $(n$-$C_4H_9)_2GeHCl$, $(n$-$C_4H_9)_2GeHBr$ and $(n$-$C_4H_9)_2GeHI$. This paper also presents the alkylgermanium trihalides n-$C_4H_9GeBr_3$ and n-$C_4H_9GeI_3$ and the polymeric white solid $[(n$-$C_4H_9GeO)_2O]_n$, with data for n-$C_4H_9GeCl_3$.

Experimental Results

Table I lists the boiling points, densities, refractive indices, molar refractions, analyses and distillation ranges for 8 new organogermanium compounds: n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$, n-$C_4H_9GeBr_3$, n-$C_4H_9GeH_2I$, n-$C_4H_9GeI_3$, $(n$-$C_4H_9)_2GeHCl$, $(n$-$C_4H_9)_2GeHBr$ and $(n$-$C_4H_9)_2GeHI$. There is adequate data for n-$C_4H_9GeCl_3$. A separate paragraph in the Experimental section presents the properties and analysis of the polymeric white solid $[(n$-$C_4H_9GeO)_2O]_n$.

Experimental

Equipment.—The equipment was the same as described before.[1,3]

Grignard Reaction.—Gradual addition of 1.04 l. of 1.9 *M* n-C_4H_9MgCl to 440 g. of $GeCl_4$ dissolved in 200 ml. of ether, then shaking the resultant mixture with 8 *M* HCl to extract $MgCl_2$, next separation of layers and drying of the ether layer with Na_2SO_4, and finally fractional distillation furnished 130 g. of n-$C_4H_9GeCl_3$ and 135 g. of higher boiling compounds.

***n*-Butylgermane and Di-*n*-butylgermane.**—Reaction of 100 g. of n-$C_4H_9GeCl_3$ with a solution of 19 g. of $LiAlH_4$ in 150 ml. of di-*n*-dibutyl ether, followed by direct distillation of the resultant n-$C_4H_9GeH_3$, furnished 56 g. (99% yield) of n-$C_4H_9GeH_3$. This n-$C_4H_9GeH_3$ had a peculiar odor something like that of a tin can which has stood open with some adhering food for some time; the compound had b.p. 75.6°, n^{20} 1.4207 and $d^{20}{}_4$ 1.033, all in reasonable agreement with the published data.[7] Reaction of the 135 g. of the higher boiling mixture in the paragraph above with 15 g. of $LiAlH_4$ in 600 ml. of diethyl ether ultimately furnished 54 g. of $(n$-$C_4H_9)_2GeH_2$, b.p. 76.2–76.7 at 24 mm., 19 g. of crude $(n$-$C_4H_9)_3GeH$, b.p. 68–69° at 1 mm., and 9 g. of $(n$-$C_4H_9)_4Ge$, b.p. about 115° at 1 mm. Center fraction $(n$-$C_4H_9)_2GeH_2$ had n^{20} 1.4423 and $d^{20}{}_4$ 0.977, both in agreement with previous data,[7] and also the new b.p. of 173° under 760 mm. pressure; there was a slight, agreeable odor. Storage of these hydrides, also all other products in this paper, was in sealed glass tubes.

***n*-Butyltrichlorogermane.**—Further fractional distillation of the n-$C_4H_9GeCl_3$ mentioned under Grignard Reaction above gave pure material listed as center fraction in Table I and serving for reactions.

***n*-Butyliodogermane.**—Gradual addition of 9.4 g. of powdered iodine to 6.2 g. of n-$C_4H_9GeH_3$ over a period of 2 hr. mainly at 0° and then fractional distillation furnished some unchanged n-$C_4H_9GeH_3$, then 8.4 g. (70% yield) of n-$C_4H_9GeH_2I$ and some higher boiling material. Two successive redistillations furnished a 4.2 g. center fraction n-$C_4H_9GeH_2I$ listed in Table I; the compound had a peculiar, penetrating odor.

***n*-Butyltriiodogermane.**—Gradual addition of 19 g. of iodine over 2 hr. at 0° to 6.8 g. of n-$C_4H_9GeH_3$, then addition of another 19 g. of iodine (total 38 g., with a slight color of excess iodine) at 30°, with a little heating at the end, and then distillation from copper powder gave 24.0 g. (92% yield) of clear, pale yellow n-$C_4H_9GeI_3$. *n*-Butyltriiodogermane decomposed slightly at the normal b.p. to give a yellow solid such as GeI_2 or possibly GeI_4; n-$C_4H_9GeI_3$ had a refractive index above 1.70.

***n*-Butylbromogermane.**—Storage of 7.7 g. of $HgBr_2$ and 6.2 g. of n-$C_4H_9GeH_3$ for 5 hr. at 31° and then 10 minutes of gentle reflux, followed by fractional distillation, furnished metallic mercury, 1.0 g. of unchanged n-$C_4H_9GeH_3$, 7.7 g. (78% yield) of n-$C_4H_9GeH_2Br$ and 0.5 g. of residue. Table I lists a 3.5 g. center fraction with a rather sharp and penetrating odor.

***n*-Butylchlorogermane.**—Addition of 6.0 g. of $HgCl_2$ to 6.20 g. of n-$C_4H_9GeH_3$ at 0°, with shaking and standing 1.2 hr., warming up to 25°, gave a liquid with 14.4% Cl. Thereafter, addition of 1.20 g. of $HgCl_2$ (total 7.20 g.), storage for 1 hr., slight heating and then distillation under 160 mm. pressure furnished 6.35 g. (82% yield) of n-$C_4H_9GeH_2Cl$, later redistilled to give the center fraction listed in Table I. This n-$C_4H_9GeH_2Cl$ is a colorless, mobile liquid with a very penetrating odor.

Di-*n*-butylbromogermane and Di-*n*-butylchlorogermane.—Treatment of 5.4 g. of $(n$-$C_4H_9)_2GeH_2$ with 7.15 g. of $HgBr_2$ or with 5.88 g. of $HgCl_2$—letting stand 1 hr. with 80% of the mercuric salt, then adding the remainder with gentle heat—furnished metallic mercury and 7.05 g. (92% yield) of $(n$-$C_4H_9)_2GeHBr$ or 6.07 g. (97% yield) of $(n$-$C_4H_9)_2GeHCl$. Redistillations furnished the center fractions listed in Table I. Both new compounds had weak aromatic odors.

Di-*n*-butyliodogermane.—There was a quite rapid reaction during the gradual addition of 4.12 g. of powdered iodine at 25° to 4.5 g. of $(n$-$C_4H_9)_2GeH_2$. A fractional distillation under 1 mm. pressure furnished 0.8 g. essentially $(n$-$C_4H_9)_2GeH_2$, 4.25 g. (57% yield) of crude $(n$-$C_4H_9)_2GeHI$ and approximately 2.3 g. of higher boiling material. Redistillation gave a 2.6 g. center fraction of $(n$-$C_4H_9)_2GeHI$ listed in Table I; this compound appeared to decompose slightly in the determination of b.p. at 760 mm. pressure.

***n*-Butylgermanium Oxide.**—The process included the following successive steps: shaking 7.9 g. of n-$C_4H_9GeCl_3$ twice with 24 g. portions of 8 *M* NH_4OH for 30 minutes each time, next adding 24-g. of CCl_4 and then washing with water, later drying the CCl_4 layer with Na_2SO_4, next careful evaporation of the CCl_4 in a platinum crucible on a hot-plate, finally drying for 3 hr. at 140° under 1 mm. pressure. This $[(n$-$C_4H_9GeO)_2O]_n$ weighed 4.83 g. (93% yield) before powdering with an agate mortar and pestle.

***n*-Butyltribromogermane.**—Four g. of $[(n$-$C_4H_9GeO)_2O]_n$ and 18 g. of 47% HBr upon heating to boiling on a hot-plate, then cooling and extracting with CCl_4, followed by fractional distillation furnished 4.9 g. of crude n-C_4H_9Ge-

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[7] J. Satgé, R. Mathis-Noël and M. Lesbre, *Compt. rend.*, **249**, 131 (1959).

Br_3. Retreatment of the residue—which contained mainly polymeric oxide—with 4 g. of 47% HBr gave another 1.5 g. of crude n-$C_4H_9GeBr_3$, with a residue of 1 g. Fractional distillation of all the n-$C_4H_9GeBr_3$ (6.4 g. or 67% yield) furnished a 4 g. center fraction listed in Table I. Upon shaking with a large excess of water this n-$C_4H_9GeBr_3$ hydrolyzed easily to the polymeric oxide.

Discussion

Preparative Methods.—Gradual addition of deficiencies of $HgCl_2$, $HgBr_2$ or I_2 convert n-$C_4H_9GeH_3$ or $(n$-$C_4H_9)_2GeH_2$ into the new partially substituted compounds of the $RGeH_2X$ or the R_2GeHX types, respectively. Table I lists six compounds, apparently the first examples of these types. This partial substitution is exactly like that of the alkylsilanes already demonstrated.[3-6] Although there are fewer known germanium compounds, 6 in all, of these types, several comparisons with the corresponding alkylhalosilanes are possible. First, the corresponding alkylgermanes are more reactive toward halogens or halides. Second, the alkylhalogermanes of the $RGeH_2X$ type are much less reactive toward water or aqueous NaOH. Efforts to change n-$C_4H_9GeH_2Cl$ into the analogous n-$C_4H_9GeH_2OGeH_2$-n-C_4H_9 either showed incomplete reaction or destruction of some of the Ge–H bonding in treatment with aqueous NaOH; the reaction with n-$C_4H_9SiH_2Cl$ and pure water proceeds satisfactorily.[6]

Molar Refractions.—Table I lists calculated molar refractions, based on the apparently reliable Ge–H bond refraction of 3.59[7] and some comparatively approximate bond refractions for Ge–Cl, Ge–Br and Ge–I.[8] The present paper merely follows the existing[8] values for the germanium to halogen bond, with intention to improve these values later.

[8] A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954); A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 531 (1952).

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, DEPARTMENT OF CHEMISTRY, BALTIMORE 18, MD.]

Nitrogen Chemisorption at −195° on Reduced Iron and Cobalt Oxides

BY R. J. KOKES

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Evidence has been presented for chemisorption of nitrogen at −195° on reduced iron and cobalt oxides. For iron the amount of nitrogen chemisorbed corresponds to 10 to 20% of V_m, as determined by the BET method; for cobalt this figure is 50 to 60%. These conclusions imply that nitrogen surface area determinations on metallic catalysts may be subject to large errors. If allowance is made for such errors it appears that carbon monoxide chemisorption on iron, cobalt and nickel is 1.1 to 1.2 times the correct V_m. value.

Although the validity of the formal theory of physical adsorption of gases on solid surfaces[1] has been questioned,[2] the now classic experiments of Emmett and Brunauer[3] provide ample evidence that physical adsorption provides a valid basis for the determination of surface area. Today, it is often forgotten that these investigators[1,3] clearly stated that this method is not valid when (a) the adsorbate is strongly, *i.e.*, chemically adsorbed and (b) when the pore structure of the adsorbent is such that all the surface is not accessible to the adsorbate. In these studies[3] it was found that for a wide variety of solids, nitrogen chemisorption at −195° was virtually non-existent; hence, nitrogen has become a preferred adsorbate for such measurements of surface area. In recent years, researches on evaporated metal films have shown that nitrogen chemisorption does occur on many transition metals between −195° and room temperature,[4-6] and this led Beeck[4] to question the validity of nitrogen surface areas on metals. At that time, however, evaporated metal films and catalysts prepared by reduction of oxides appeared to be different in many respects so that the low temperature nitrogen chemisorption on films was accepted as another difference between ultra-clean metals, *i.e.*, evaporated metal films, and metals prepared by reduction of oxides.

There seems to be a growing body of data which suggests that carefully reduced nickel oxides are, in fact, similar to the nickel films.[7] In particular, recent investigations[8,9] strongly suggest that reduced nickel oxides exhibit the same type of weak nitrogen chemisorption at −195° observed by Beeck[4] on evaporated nickel films. These results suggest that other transition metals prepared by reduction of the oxide also may show nitrogen chemisorption at −195°. If this be the case, it would not only provide additional evidence that results with reduced oxides are indeed comparable with those found for films but would also reemphasize the fact[3,4,8,9] that indiscriminate use of nitrogen for determinations of surface area can lead to large errors. In this paper we have examined reduced iron and cobalt oxides for nitrogen chemisorption.

Experimental

Catalyst Preparation.—The procedure for the preparation of the iron catalyst was similar to that described by Emmett and Gray.[10] A 10% excess of ammonia was added to a solution of 200 g. of $Fe(NO_3)_3 \cdot 9H_2O$ in two liters of distilled water. The precipitate was coagulated by boiling the slurry

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[5] E. Greenhalgh, M. Slack and B. M. W. Trapnell, *Trans. Faraday Soc.*, **52**, 865 (1956).

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[8] R. J. Kokes and P. H. Emmett, THIS JOURNAL, **80**, 2082 (1958).

[9] R. J. Kokes and P. H. Emmett, *ibid.*, **82**, 1037 (1960).

[10] P. H. Emmett and J. B. Gray, *ibid.*, **66**, 1338 (1944).