tue of possession of unfilled d orbitals by the X atoms. The stability of bonds involving d orbitals usually increases with increase in the atomic number of X. Likewise, the formation of dimers should be sterically favored by increase in size of X. Therefore, the stability of the dimers should be: $BrF_3 > ClF_3$, $IF_5 > BrF_5$ and $MF_3 > MF_5$. If it is assumed then that dimerization is the mechanism of fluorine exchange in the halogen fluorides, the rates of fluorine exchange might be expected to decrease in the order $BrF_3 > ClF_3 > IF_5 > BrF_5$. The results of the *n–m–r* study of exchange in halogen fluorides confirm this ordering for relative rates of exchange and thus indicate dimerization to be the mechanism for exchange in these systems.

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Reactions of Triethylgermanium Hydride with Salts of Transitional Elements and with Organic Haloacids

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Triethylgermanium hydride reduces salts of certain transitional elements either to a lower oxidation state or sometimes to the free metal. These reductions apparently occur with transitional elements in which the oxidation potential $E°$ for the highest oxidation state present—such as Ti(III) to Ti(IV)—has a value of -0.06 volt or less; as expected, no reduction of $CdCl_2$ occurs. Triethylgermanium hydride yields the corresponding new esters when heated with the strong acids CF_3COOH, C_2F_5COOH and n-C_3F_7COOH; the weak acid CH_3COOH does not react at an appreciable rate. Moreover, triethylgermanium hydride reduces certain organic chloroacids, bromoacids or iodoacids. This paper includes new densities and refractive indices for triethylgermanium chloride, bromide, iodide and hydride.

This paper describes the previously unknown reaction of triethylgermanium hydride with salts of the transitional elements, and also with organic haloacids. Triethylgermanium hydride first was prepared by three successive reactions[1]

$$2(C_2H_5)_3GeBr + 2Na \longrightarrow (C_2H_5)_3GeGe(C_2H_5)_3 + 2NaBr$$

$$(C_2H_5)_3GeGe(C_2H_5)_3 + 2Li \longrightarrow 2LiGe(C_2H_5)_3$$

$$LiGe(C_2H_5)_3 + NH_2 \longrightarrow (C_2H_5)_3GeH + LiNH_2$$

The preparation of $C_2H_5SiH_3$[2] from $C_2H_5SiCl_3$ and $LiAlH_4$ and also the preparation of tricyclohexylgermanium hydride[3] from $(C_6H_{11})_3GeCl$ and $LiAlH_4$ suggested the one-step preparation of $(C_2H_5)_3GeH$

$$4(C_2H_5)_3GeCl + LiAlH_4 \longrightarrow 4(C_2H_5)_3GeH + LiCl + AlCl_3$$

which we have demonstrated.

There is little information on the reactions of organogermanium hydrides in the literature. Typically, triphenylgermanium hydride yields $(C_6H_5)_3GeBr$ in reaction with bromine $(C_6H_5)_3GeH + Br_2 \rightarrow (C_6H_5)_3GeBr + HBr$ or with concentrated hydrobromic acid $(C_6H_5)_3GeH + HBr \rightarrow (C_6H_5)_3GeBr + H_2$.[4]

Twenty-one reactions in Table I of the present paper indicate that $(C_2H_5)_3GeH$ is a fairly reactive compound. The corresponding oxide $[(C_2H_5)_3Ge]_2O$ reacts easily with the *weak* acid CH_3COOH to yield $(C_2H_5)_3GeOCOCH_3$,[5] while $(C_2H_5)_3GeH$ and CH_3COOH react very slowly during reflux, if at all. Reflux with *strong* acids such as hydrochloric, sulfuric or trifluoroacetic converts the $(C_2H_5)_3GeH$ into the corresponding halide or ester easily; *weaker* CHF_2COOH in a 2-hour reflux furnishes a 60% yield of ester, while *still-weaker* CH_2FCOOH furnishes a 20% yield of ester at most.

Unlike acetic acid, which contains a much lower concentration of acetate ions, mercuric acetate reacts completely with $(C_2H_5)_3GeH$ in 15 minutes of reflux, with formation of metallic mercury.

In the reaction listed in Table I, there is a reduction of the iodoacetic acid to acetic acid.

$$(C_2H_5)_3GeH + ICH_2COOH \longrightarrow (C_2H_5)_3GeI + CH_3COOH$$

Similar reductions occur in reactions with CCl_3COOH and CBr_3COOH, but none occurs with completely fluorinated CF_3COOH, C_2F_5COOH and n-C_3F_7COOH. All this appears consistent with the following bond energies in kcal./mole: C–F, 107; C–H, 87; C–Cl, 67; C–Br, 54; C–I, 46.

A related exchange of Si–H and C–Cl occurs when $AlCl_3$ catalyst is present.[6]

$$(C_2H_5)_3SiH + n\text{-}C_6H_{13}Cl \longrightarrow (C_2H_5)_3SiCl + n\text{-}C_6H_{14}{}^{6}$$

Fourteen reactions of $(C_2H_5)_3GeH$ with salts or halides of transitional elements, listed in Table I, and the previously reported reaction of $(i\text{-}C_3H_7)_2GeH_2$ with $AgOCOCH_3$[7] to yield $(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$ and silver, suggest the following three conclusions.

1. These reductions apparently occur with transitional elements in which the oxidation potential $E°$ for the next-highest to the highest oxidation state present—such as Ti(III) to Ti(IV)—has a value between approximately -0.06 and -2.0 v. As expected, refluxing $(C_2H_5)_3GeH$ with $CdCl_2$ brings no reduction to Cd, since $E°$ for Cd is $+0.40$ v. Although there is no available oxidation potential, $E°$, for germanium, the failure of metallic germanium to react with hydrochloric acid

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(1) C. A. Kraus and E. A. Flood, THIS JOURNAL, **54**, 1635 (1932).

(2) A. E. Finholt, *et al.*, *ibid.*, **69**, 2692 (1947).

(3) O. H. Johnson and W. R. Nebergall, *ibid.*, **71**, 1720 (1949).

(4) C. A. Kraus and L. S. Foster, *ibid.*, **49**, 457 (1927).

(5) H. H. Anderson, *ibid.*, **72**, 2089 (1950).

(6) F. C. Whitmore, *et al.*, *ibid.*, **69**, 2108 (1947).

(7) H. H. Anderson, *ibid.*, **78**, 1692 (1956).

TABLE I

REACTIONS OF $(C_2H_5)_3GeH$, 1.30 G./RUN WITH SALTS OF TRANSITIONAL ELEMENTS, ALSO ACIDS

Salt or acid at start			Reaction products				
			Chief product				
Compound	Wt., g.	Reflux, min.	Compound	B.p., °C.	Wt., g.	Yield, %	Other products
$CuBr_2$	1.70	60	$(C_2H_5)_3GeBr$	191	1.77	90	$Cu_2Br_2{}^a + H_2$
$KAuCl_4$	0.98	15	$(C_2H_5)_3GeCl$	176	1.49	95	$KCl + Au + H_2$
$HgCl_2$	1.07	10	$(C_2H_5)_3GeCl$	176	0.85	55	$Hg + HCl^b + H_2{}^c$
Hg_2Cl_2	3.20	35	$(C_2H_5)_3GeCl$	175	1.42	90	$Hg + HCl^b + H_2{}^c$
$HgBr_2$	3.20	45	$(C_2H_5)_3GeBr$	191	1.88	98	$Hg + H_2 + HBr^{c,d}$
HgI_2	3.90	15	$(C_2H_5)_3GeI$	212	2.30	99	$Hg_2I_2{}^a + H_2$
$HgSO_4$	1.11	15	$[(C_2H_5)_3Ge]_2SO_4$	336	1.14	70	$Hg + H_2 + [(C_2H_5)_3Ge]_2O^{c,e}$
$Hg(OCOCH_3)_2$	1.20	15	$(C_2H_5)_3GeOCOCH_3$	191	1.07	60	$Hg + H_2 + CH_3COOH^f$
$TiCl_4$	1.23	40	$(C_2H_5)_3GeCl$	173	1.07	70	$TiCl_3{}^g + TiCl_2{}^c + H_2$
$VOCl_3$	1.28	2	$(C_2H_5)_3GeCl$	175	1.50	95	$VOCl_2{}^h + VOCl^{a,c} + H_2$
CrO_2Cl_2	0.54	5	$(C_2H_5)_3GeCl$	174	0.70	45	$Cr_2O_3{}^{a,i} + H_2 + H_2O^c$
$KMnO_4{}^j$	.34	0	$[(C_2H_5)_3Ge]_2O$	252	0.37	28	$MnO_2{}^{a,j} + KOH$
$PdCl_2$	.66	10	$(C_2H_5)_3GeCl$	176	1.30	88	$Pd + H_2$
K_2PtCl_6	.98	120	$(C_2H_5)_3GeCl$	175	1.47	95	$KCl + Pt + H_2$
CF_3COOH	1.46	180	$(C_2H_5)_3GeOCOCF_3{}^k$	183	2.09	95	H_2
C_2F_5COOH	1.80	70	$(C_2H_5)_3GeOCOC_2F_5{}^k$	190	2.52	99	H_2
$n\text{-}C_3F_7COOH$	1.60	60	$(C_2H_5)_3GeOCO\text{-}n\text{-}C_3F_7{}^k$	201	2.88	97	H_2
CCl_3COOH	0.37	90	$(C_2H_5)_3GeCl$	175	1.24	80	$CH_3COOH + (C_2H_5)_3GeOCOCH_2Cl^{c,l}$
CBr_3COOH	0.75	90	$(C_2H_5)_3GeBr$	190	1.80	94	CH_3COOH
CH_2ICOOH	1.40	60	$(C_2H_5)_3GeI$	212	2.17	94	CH_3COOH^m
100% H_2SO_4	0.37	5	$[(C_2H_5)_3Ge]_2SO_4$	343	1.10	70	$H_2 + [(C_2H_5)_3Ge]_2O^{c,n}$

[a] Compound insoluble in water. [b] HCl accounted for 60% of hydrogen. [c] Present as a minor component. [d] HBr accounted for 10% of hydrogen. [e] B.p. 253°; weight 0.28 g. [f] Weight 0.16 g. [g] Reaction gave water-soluble violet $TiCl_3$ and some brown $TiCl_2$. [h] Reaction gave water-soluble green $VOCl_2$ and some brown, water-insoluble VOCl. [i] Light-green solid. [j] Reaction performed in 25 ml. of acetone solution. Brown solid produced liberated chlorine from hydrochloric acid. [k] New compound, described in Experimental. [l] B.p. 228°, neut. equiv., 253. Reaction produced 5 ml. of hydrogen. See: H. H. Anderson, *J. Org. Chem.*, **20**, 900 (1955). [m] Neut. equiv. 66; b.p. 119°. [n] B.p. 254°; weight 0.4 g.

suggests that $E°$ for Ge(0) to Ge(II) has a value just below 0.0 v. This value for $E°$ is consistent with the 14 reactions in Table I.

2. Subject to the stoichiometry, of course, the reductions apparently proceed as far as the oxidation potentials for the various oxidation states allow: platinum, palladium and gold compounds are reduced to the metals; when mercuric salts are in excess at the start Hg(II) is reduced only to Hg(I), while a deficiency of mercuric salt allows reduction to metallic mercury; in a single experiment excess Cu(II) is reduced to Cu(I); Ti(IV) is reduced partly to Ti(III) and partly to Ti(II), in the ratios given in Table I; V(V) in $VOCl_3$ is reduced partly to V(IV) in $VOCl_3$ and partly to V(III) in VOCl in the ratios in Table I; the limits of reduction appear to be the compounds $TiCl_2$, VOCl, Cr_2O_3, MnO_2 and Cu_2Br_2.

3. The yields are fairly high, with a median of 90% in Table I. Higher yields should result from use of more $HgCl_2$ and more $Hg(OCOCH_3)_2$, while higher yields may result from use of more CrO_2Cl_2 and more $KMnO_4$.

Related experiments with halides and $(C_2H_5)_3SnH$ are essentially complete, and work with halides and $(C_2H_5)_2SiH_2$ is in process.

Experimental

Equipment for all reactions included distilling units with 10/30 standard taper ground joints on all units and accessories, micro-pycnometers, a 0.02460-ml. micropipet for the measurement of liquids and the subsequent titration of the available acidity,[8] transfer micropipets, and some very small distilling units recently designed for fractional distillation of one ml. of liquid or less.

Triethylgermanium Hydride.—Addition of 76 g. of $(C_2H_5)_3GeCl$ over a period of 30 minutes to a solution of 15 g. of $LiAlH_4$ in 500 ml. of dry ether was followed by two hours of reflux. After slow addition of water until two layers remained, addition of 300 ml. of 3 *M* H_2SO_4 and shaking caused a persistent slow evolution of hydrogen—a later experiment (Table I)—showed the formation of $[(C_2H_5)_3Ge]_2SO_4$ from $(C_2H_5)_3GeH$ and H_2SO_4. Separation of layers within ten minutes, then washing the ether layer with water, followed by drying with Na_2SO_4 and then careful distillation of the ether, finally furnished 49 g. of $(C_2H_5)_3GeH$, a yield of 79%. As explained previously, the crude product contained some high-boiling material, largely $[(C_2H_5)_3Ge]_2SO_4$. Center-fraction $(C_2H_5)_3GeH$ boiled at 124° under 760 mm., and had n^{20} 1.438_2 and $d^{20}{}_4$ 1.009, values not previously reported. Storage was in sealed tubes bearing a minimum of air.

Starting materials were commercial products, except for $KAuCl_4$, $VOCl_3$, CrO_2Cl_2 and K_2PtCl_6; all the inorganic solids were powdered. The acid CCl_3COOH required removal of water absorbed from the air. Precautionary fractional distillations of C_2F_5COOH and $n\text{-}C_3F_7COOH$ (Peninsular Chemicals Co., Gainesville, Fla.) were performed. Aldrich Chemical Co., Milwaukee, Wisconsin, furnished the CBr_3COOH.

Reactions of $(C_2H_5)_3GeH$.—The general method of reaction consisted of either (1) introducing the dry solid such as HgI_2 into the special distilling unit first, and then slowly adding the $(C_2H_5)_3GeH$ or (2) introducing the $(C_2H_5)_3GeH$ first, and then slowly adding the liquid such as $VOCl_3$; in some cases cooling of the unit was necessary. Reflux was achieved by means of an electrical heating cone.

Identification of the Chief Organogermanium Product in Table I.—The organogermanium product was separated from the other products by first pipetting when Hg metal was present, or centrifuging and washing when MnO_2 was present, or distillation in the other cases, often under reduced pressure. Centrifuging and pipetting removed small amounts of Hg(I) salts from distillates. Fractional distillation to remove all lower-boiling components such as

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[8] H. H. Anderson, THIS JOURNAL, **71**, 1801 (1949); *Anal. Chem.*, **24**, 579 (1952).

excess $(C_2H_5)_3GeH$ was followed by collection or the main $(C_2H_5)_3GeX$ derivative; when necessary, the main $(C_2H_5)_3GeX$ derivative was redistilled in special small equipment.

Ultimate identification consisted of determining the boiling point (listed in Table I), $d^{20}{}_4$, n^{20} and the halogen, acetate or sulfate content of the compound, and comparison with available known values.[1] The b.p. of $(C_2H_5)_3GeOCOCH_3$[5] is 190.5° and that of $[(C_2H_5)_3Ge]_2SO_4$[9] is 342°. The reactions with H_2SO_4 and CCl_3COOH furnished chief organogermanium products with selected fractions only 96% pure, while the reaction with $TiCl_4$ gave a fraction only 91% pure. All other reactions furnished selected fractions of chief products that were at least 98% pure.

Identification of Other Products in Table I.—Visual observation was enough to establish the formation of the metals; other tests included solubility in water, the inflammability of hydrogen, the b.p. of acetic acid, colors and sometimes odor.

New Compounds.—Two liquid phases were originally present in each preparation of the three fluoroesters listed in Table I; after rejecting the lowest boiling 40% of the individual ester, the next 45% served for measurements. Triethylgermanium trifluoroacetate, $(C_2H_5)_3GeOCOCF_3$, distilled under 760 mm. pressure, had b.p. 183° under 760 mm., n^{20} 1.402 and $d^{20}{}_4$ 1.272. *Anal.* Calcd. for $(C_2H_5)_3GeOCOCF_3$: mol. wt., 272.8; $OCOCF_3$, 41.4. Found: mol. wt. (camphor), 264; $OCOCF_3$, 42.0. Triethylgermanium pentafluoropropionate, $(C_2H_5)_3GeOCOC_2F_5$, distilled at 115–116° under 21 mm., had b.p. 189.6° under 760 mm., n^{20} 1.384_4 and $d^{20}{}_4$ 1.324. *Anal.* Calcd. for $(C_2H_5)_3GeOCOC_2F_5$: mol. wt., 322.8; Ge, 22.5; $OCOC_2F_5$, 48.6. Found: mol. wt., 338; Ge, 22.5; $OCOC_2F_5$, 48.2. Triethylgermanium heptafluoro-*n*-butyrate, $(C_2H_5)_3GeOCO\text{-}n\text{-}C_3F_7$, distilled at 124–125° under 66 mm., had b.p. 201.0° under 760 mm., n^{20} 1.378_0 and $d^{20}{}_4$ 1.383. *Anal.* Calcd. for $(C_2H_5)_3GeOCO\text{-}n\text{-}C_3F_7$: mol. wt., 372.8; Ge, 19.5; $OCO\text{-}n\text{-}C_3F_7$, 57.2. Found: mol. wt., 393; Ge, 19.9; $OCO\text{-}n\text{-}C_3F_7$, 57.4.

New Data on Known Compounds.—Reaction of pure $[(C_2H_5)_3Ge]_2O$ with an excess of aqueous halogen acid, with drying and fractional distillation, furnished center fractions of halides with the following previously unreported properties: $(C_2H_5)_3GeCl$, n^{20} 1.464_3, $d^{20}{}_4$ 1.175; $(C_2H_5)_3GeBr$, n^{20} 1.489_2, $d^{20}{}_4$ 1.412; $(C_2H_5)_3GeI$, n^{20} 1.528, $d^{20}{}_4$ 1.608. All four boiling points agreed reasonably with the published b.p. under 760 mm. pressure[1]: $(C_2H_5)_3GeCl$, 175.9°; $(C_2H_5)_3GeBr$, 190.9°; $(C_2H_5)_3GeI$, 212.3°; $(C_2H_5)_3GeH$, 124.7°.

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(9) H. H. Anderson, THIS JOURNAL, **72**, 194 (1950).