[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Boron Hydrides. V. Methanolysis of Sodium Borohydride[1]

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The reaction of sodium borohydride with methanol produces hydrogen gas and sodium tetramethoxyboron. The reaction is first order in the borohydride concentration. The addition of acid increases the rate while basic materials such as sodium methoxide and sodium carbonate decrease the rate of methanolysis. At 25°, $-d(BH_4^-)/dt = 1.6 \times 10^7 (BH_4^-)(CH_3OH_2^+) + 1.1 \times 10^{-7} (BH_4^-)(MeOH)$ mole l.$^{-1}$ sec.$^{-1}$. The data have been compared with the data on hydrolysis in aqueous medium. The effect of sodium methoxide upon the methanolysis explains the variable results of previous investigations. With proper control of temperature and basicity, methanol can be used as a medium for reducing ketones to secondary alcohols. The slow addition of one mole of ketone to a basic solution of borohydride gives one mole of alcohol and three moles of hydrogen gas. This is explained in terms of the great reactivity of $(RO)_xBH_{4-x}$ toward methanolysis.

Introduction

Following the discovery of sodium borohydride by Schlesinger and Brown[3] during World War II, there has been an ever increasing use of this unique reducing agent.[4] It is highly soluble in water and very stable in aqueous alkaline solution.[5-8] Sodium borohydride is also very soluble in methyl alcohol (16.4 g./100 g. of methanol)[9] but reacts producing hydrogen and sodium tetramethoxyboron

$$NaBH_4 + 4CH_3OH \longrightarrow NaB(OCH_3)_4 + 4H_2 \quad (1)$$

The rate reaction 1 has been estimated manometrically by Brown[10] who observed that four moles of hydrogen were produced in twenty-four minutes at 60°. Brown and Ichikawa[11] have recently studied the methanolysis at 0° using the iodate analysis.[12] In their study the methanolysis occurred much more readily. The first-order rate constant was 5.8×10^{-4} sec.$^{-1}$ at 0° which represents a twenty-minute half-time. The conclusion[4,11] has been reached that methanol is a poor medium for reductions because of the relative large loss of reducing agent by reaction with the solvent. Chaikin and W. G. Brown[13] originally emphasized the use of methanol as a medium for reduction of ketones and aldehydes. H. C. Brown[4] has more recently emphasized the use of ethanol (4.0 g. of $NaBH_4$/100 g. of solvent)[9] or ethanol–water for reduction in homogeneous solution as the ethanolysis is much slower ($k_1 \cong 1 \times 10^{-7}$ sec.$^{-1}$ at 0°,[11] $k_1 = 2.9 \times 10^{-6}$ sec.$^{-1}$ at 25°[14]).

Chaikin and W. G. Brown[13] successfully reduced materials with sodium borohydride in methanol in high yields even though some of the reductions are quite slow. Over the passage of twelve years,[10,11,13] sodium borohydride has become more unstable in methanol. In continuing our studies on the kinetics and mechanisms of boron hydride reactions and at the strong suggestion of H. C. Brown, we have reinvestigated the methanolysis reaction.

Results and Discussion

Reaction Order.—The reaction of borohydride and methanol has been studied by noting the volume of hydrogen produced and by measuring the loss of reducing power of the solution with the iodate technique. One mole of borohydride disappears and four moles of hydrogen are produced.

$$\frac{-d(BH_4^-)}{dt} = \frac{1}{4}\frac{d(H_2)}{dt} = k_1(BH_4^-) \quad (2)$$

The reaction order is unity in borohydride ion over a fifteen-fold variation (1.00×10^{-3} to 14.7×10^{-3} *M*) in initial concentration of sodium borohydride *provided that the sodium borohydride is quite pure*. Using material from a freshly opened bottle which analyzed about 98% pure, the observed first-order rate constant depended upon the initial amount of sodium borohydride present. Thus some contaminant in the impure sample decreases the rate of hydrolysis. The rate suppression is a linear function of the initial concentration of borohydride.

Unlike the reaction of borohydride and pure water

$$BH_4^- + H_3O^+ + 2H_2O \longrightarrow 4H_2 + H_3BO_3 \quad (3)$$

which consumes acid and causes an upward drift in the *p*H and a downward drift in the rate,[11] the reaction of borohydride and methanol (reaction 1) does not change the acidity of the medium. Sodium tetramethoxyboron has little effect upon the rate and thus fairly good first-order kinetics are observed. However, the addition of acidic materials like perchloric acid produces a nearly instantaneous destruction of the borohydride ion. Even boric acid greatly accelerates the decomposition (Table I). The reaction order in acid cannot be conveniently determined due to the rapidity of

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[1] Paper IV, R. E. Davis, *J. Am. Chem. Soc.*, **84**, 892 (1962).

[2] National Science Foundation Undergraduate Summer Research Participant, 1961. Taken from the senior thesis of J. A. Gottbrath.

[3] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *J. Am. Chem. Soc.*, **75**, 199 (1953); H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953).

[4] For a recent review see H. C. Brown, *J. Chem. Ed.*, **38**, 173 (1961).

[5] For a comprehensive survey of the literature and a study of the kinetics of hydrolysis, the reader is referred to recent papers.[6-8]

[6] R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5449 (1960).

[7] R. E. Davis, C. L. Kibby and C. G. Swain, *ibid.*, **82**, 5450 (1960).

[8] R. E. Davis, E. Bromels and C. L. Kibby, *ibid.*, **84**, 885 (1962).

[9] "Sodium Borohydride, Potassium Borohydride, A Manual of Techniques," Metal Hydrides, Inc., Beverly, Mass., 1958, p. 9.

[10] H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955). These authors give a table from which the first half-time of about 6 minutes can be estimated at 60°. A plot of their data shows that the first-order rate constant increases with time. This could be due to the large heat of reaction of borohydride or changes in the medium during reaction. The large ΔH has received comment in a previous study.[8]

[11] H. C. Brown and K. Ichikawa, *ibid.*, **83**, 4372 (1961).

[12] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

[13] S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).

[14] Unpublished data of R. E. D.

the reaction. However, the addition of sodium methoxide produces a marked reduction in the observed first-order rate constant. The data can be explained in terms of the reactions

$$2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^- \quad (4)$$

$$CH_3OH_2^+ + BH_4^- \xrightarrow{k_2} \text{products} \quad (5)$$

$$CH_3OH + BH_4^- \xrightarrow{k_3} \text{products} \quad (6)$$

Thus

$$\text{rate} = k_1(BH_4^-) = k_2(CH_3OH_2^+)(BH_4^-) + k_3(CH_3OH)(BH_4^-) \quad (7)$$

Defining K_p as the ion product of methanol eq. 7 becomes

$$\text{rate} = \frac{k_2K_p(BH_4^-)}{(CH_3O^-)} + k_3(CH_3OH)(BH_4^-) \quad (8)$$

These equations are completely equivalent to the general acid catalysis observed in aqueous solution.[6-8]

The value of k_1, the observed first-order constant, depends upon the purity of the sodium borohydride, its past history and the purity of the methanol. Further examination of these features of the reaction explains the variable results reported in the literature.[9,10,11,13] Traces of sodium methoxide greatly increase the stability of borohydride to methanolysis. *If an organic substrate can tolerate the presence of methoxide, methanol can be used as a solvent.*[15]

Chaikin and Brown[13] carefully stated that sodium borohydride used in their study was about 90% pure. As the purity of sodium borohydride has increased during the past few years in commercial samples, the sodium methoxide concentration has been greatly reduced. Thus the decreasing stability of the borohydride ion in methanol as a function of time is due to the increased purity of commercial samples.

Thus cyclohexanone in methanol can be reduced in good yield by adding slowly a solution of sodium borohydride in methanol containing sodium methoxide. Very little hydrogen gas, the product of reaction with the solvent, is produced. Likewise benzophenone, a ketone which is reduced slowly by borohydride,[16] can be reduced successfully to benzhydrol.

Sodium carbonate, another possible impurity in borohydride samples, will also decrease the rate of methanolysis. Sodium borate added as the hydrate salt actually increases the rate slightly. Perhaps this is due to the addition of small amounts of water as added water does increase the initial rate of hydrolysis but the rate then decreases slowly throughout the course of reaction.

Sodium chloride increases the rate. As a first approximation based on activity coefficients, a salt should increase the ion product of methanol, thus increasing the concentration of $CH_3OH_2^+$. But an inert salt should decrease the rate of reaction of a uni-positive species with a uni-negative species. If the charge is completely neutralized in the rate step (5), the effect should just cancel. However, there is a positive salt effect, which suggests that the charges are not completely neutralized in the rate step. Thus by another line of argument,[6-8] the activated complex formed from a general acid (HA_j) still contains a protonic hydrogen and a hydridic borohydride

$$HA_j + BH_4^- \rightleftharpoons \begin{bmatrix} H^-BH_4^- \\ A_j^- \end{bmatrix}^{\ddagger} \longrightarrow H_2 + BH_3 + A_j^-$$

The activated complex is ionic and again a stable HBH_4 molecule has been ruled out.[6-8]

TABLE I

SODIUM BOROHYDRIDE IN METHANOL

$T = 25.00 \pm 0.01°$

Expt.[a]	Sample[b]	Conditions[c]	$k_1 \times 10^3$ sec.$^{-1}$ [d]
1	A		1.31 ± 0.07[h]
2	A[g]	2.58% water[e]	1.67 ± .10[f]
3	A[g]	5.07% water[e]	2.54 ± .15[f]
4	A[g]	13.88% water[e]	4.32 ± .19[f]
5	A[g]	0.05 M $HClO_4$	>690[j]
6	A[g]	0.05 M H_3BO_3	> 69[j]
7	A[g]	3.70×10^{-3} M $NaOCH_3$	0.134 ± 0.009
8	B[g]	1.45×10^{-3} M $NaOCH_3$	.203 ± .010
9	B[g]	1.87×10^{-3} M $NaOCH_3$	.182 ± .010
10	B[g]	3.75×10^{-3} M $NaOCH_3$	.128 ± .009
11	B[g]	5.55×10^{-3} M $NaOCH_3$	.075 ± .007
12	B	1.00×10^{-3} M $NaOCH_3$	.413 ± .010
		$49.0 \times 10^{-3} M$ NaCl	
		5.00×10^{-3} M $NaOCH_3$	.0964 ± 0.002
		45.00×10^{-3} M NaCl	
		25.0×10^{-3} M $NaOCH_3$	.0394 ± .001
		25.1×10^{-3} M NaCl	
		50.0×10^{-3} M $NaOCH_3$	.0340 ± .001
		$T = 0.00 \pm 0.01°$	
13	A		0.45 ± 0.05[i]
14	A		.434 ± .029[h]
15	A[g]	0.01 M NaCl	.475 ± .024
		0.03 M NaCl	.49 ± .03
16	C		2.7 ± .4
17	A	.005 M borax	0.92 ± .08
		.011 M borax	1.4 ± .3[f]
		.015 M borax	4.0 ± .3[f]
18	A	.01 M H_3BO_3	>90[j]
19	B	$.69 \times 10^{-3}$ M $NaOCH_3$	0.072
		1.51×10^{-3} M $NaOCH_3$	.025
		2.19×10^{-3} M $NaOCH_3$	.0130
		9.1×10^{-3} M $NaOCH_3$	.008

Summary of data: k at 25°

$k_2K_p = 3.57 \pm 0.20 \times 10^{-7}$; $E_a = 6.8 \pm 0.4$ kcal./mole

$k_2 = 1.6 \pm 0.3 \times 10^7$ M^{-1} sec.$^{-1}$

$k_3 = 1.09 \pm 0.13 \times 10^{-7}$ M^{-1} sec.$^{-1}$; $E_a = 20 \pm 2$ kcal./mole[k]

[a] Average of at least three separate kinetic runs. [b] Sample of sodium borohydride: A, from a freshly opened bottle of a commercial sample; B, recrystd. from diglyme; C, sample B exposed to water vapor. [c] Pure methanol unless stated otherwise; iodate analysis unless stated otherwise (i). [d] First-order rate constant with an estimate of σ. [e] Weight percentage water in methanol. [f] Initial rate constant, rate constant then decreases with time. [g] Initial concn. of sodium borohydride is 6.40×10^{-3} M. [h] Initial concn. of sodium borohydride has been varied 7-fold. [i] Manometric. [j] Too fast to measure. [k] Empirical activation energies calcd. from observed rate constants.

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(15) Enough sodium methoxide should be added to have a residual concentration of about 10^{-2} M. As a rough estimate one can use sodium methoxide equal to 10% by weight of the sodium borohydride added.

(16) H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

Subsequent steps of the reaction cannot be rate controlling. Otherwise hydrogen gas would be evolved stepwise and one would not observe that the rate of loss of borohydride ion is equal to the rate of production of four moles of hydrogen. Since one can only obtain definite information on reactions occurring prior to the rate-determining reaction by kinetic methods, one can only speculate as to the subsequent steps.

Various intermediates can be suggested. The first intermediate may be solvated borine,[6-8] $CH_3OH \cdot BH_3$, or monomethoxyborohydride,[4] $CH_3OBH_3^-$. The alkoxyborohydrides have been postulated by Brown[4,11,16] to be intermediates in the reduction of ketones with borohydride. Subsequent reactions could produce dimethoxyborohydride, $(CH_3O)_2BH_2^-$, and trimethoxyborohydride, $(CH_3O)_3BH^-$. Sodium trimethoxyborohydride is a known compound which is prepared from sodium hydride and trimethyl borate. This compound undergoes a rapid disproportionation in aprotic solvents[17] forming sodium borohydride and sodium tetramethoxyborohydride. The triisopropoxyborohydride ion is an extremely reactive reducing agent in isopropyl alcohol, reducing acetone instantaneously.[18]

One set of experiments conclusively demonstrates that the intermediates are more reactive than borohydride toward reducing methanol. A ketone (cyclohexanone) was added very slowly to a basic solution of borohydride in methanol. When one mole of ketone had been added, three moles of hydrogen had been liberated. The solution was quite basic so very little hydrogen resulted from solvent decomposition of borohydride. The first step of the reaction would be

$$R'_2C{=}O + BH_4^- \xrightarrow{k} ROBH_3^- \qquad (9)$$

$$R = R'_2CH$$

As the addition of ketone is very slow, the concentration of ketone is very low at any given time. The intermediate finds very little ketone to reduce. The fact that one mole of ketone gives one mole of alcohol (cyclohexanol) with production of three moles of hydrogen means that $ROBH_3^-$ is destroyed by reducing the methanol which is in large excess. The rate expression for hydrolysis of $ROBH_3^-$ is not known, but by analogy would be

$$-d(ROBH_3^-)/dt = k_i(ROBH_3^-)(CH_3OH_2^+) + k_j(ROBH_3^-)(CH_3OH) \qquad (10)$$

Perhaps k_i is larger than k_2 ($k_2 = 1 \times 10^7\ M^{-1}$ sec.$^{-1}$). The upper limit of k_i would be about $10^9\ M^{-1}$ sec.$^{-1}$ which is the rate constant for a diffusion-controlled process. Likewise k_j could be larger than k_3. Nevertheless, at low ketone concentrations a term $k_a(R'_2CO)(ROBH_3^-)$ must be small.

An alkoxyborohydride is a more reactive reducing agent because of the electron release from the oxygen onto the boron which increases the hydridic character of the hydrogen. It is of interest to note that the reactivity of the intermediates must differ and that their steric and electronic requirements are also changing during the course of reaction. These topics will be considered in later papers in this series. The present data now allow consideration of the stereochemistry of the reduction of ketones by borohydride ion *alone* without complications due to the reduction of the carbonyl by the alkoxyborohydrides.

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Experimental

Materials.—Sodium borohydride was obtained from Metal Hydrides, Inc. Some material was recrystallized from diglyme and stored in sealed tubes (analysis 99.9%) or better). A portion of the purified borohydride was allowed to stand in the air until the crystals looked wet.

Another sample was taken from a freshly opened bottle which assayed 98.2%. Another sample was taken from an old bottle opened two years ago (96%). Each sample gave slightly different results.

Methanol was taken from several sources. Fisher certified reagent grade methanol was used, as well as one sample of Eastman spectro-grade methanol. Large volumes of methanol were purified by refluxing with magnesium turnings. The methanol was then distilled through a 27-plate helix-packed column. The middle fraction (b.p. 64.1° (746 mm.)) was stored in Pyrex bottles and withdrawn as needed for the kinetic experiments. The salts were of the highest purity commercially available.

Kinetics.—The iodate technique[12] has been discussed.[6-8] Aliquots were also withdrawn on a weight basis under protection of purified nitrogen as the solutions are quite effervescent and the pipets are filled with bubbles of hydrogen gas.

The manometric procedure was similar to that suggested by Daniels.[19] In each case the rate constant was obtained by graphic methods.

Reduction of Benzophenone.—Benzophenone (Matheson, m.p. 47–48°, 72.40 g., 0.400 mole) was dissolved in 300 ml. of methanol. To this solution maintained in an ice-bath was added a solution of sodium borohydride (3.814 g., 0.101 mole) and sodium methoxide (0.261 g., 4.85×10^{-3} mole) dissolved in 200 ml. of methanol. The total amount of hydrogen evolved was 0.02 mole (5% of the borohydride). Analysis of the reaction mixture using an F and M 609 gas chromatographic apparatus using both sorbitol column and a didecyl phthalate column demonstrated the presence of 0.389 mole of benzhydrol (94%) and 0.020 mole of unreacted benzophenone. Isolation produced pure benzhydrol, m.p. 67–67.5°.

Increasing the sodium methoxide to 3.00 g. (5.55×10^{-2} mole) decreased the amount of hydrogen gas produced to 0.0105 mole (2.6% of the borohydride). The yield of benzhydrol was little affected.

In an experiment with 0.261 g. of sodium methoxide, the reverse process of adding the ketone to the borohydride solution produced 0.13 mole (32%) of hydrogen.

Reduction of Cyclohexanone.—To a solution of cyclohexanone (Baker, purified, b.p. 154–155° (740 mm.), 39.26 g., 0.400 mole) in 100 ml. of methanol at 0° was added 100 ml. of a solution containing 3.785 g. (0.100 mole) of sodium borohydride with 0.378 g. (7.0×10^{-3} mole) of sodium methoxide. Some hydrogen was produced. Analysis of the reaction mixture on a 1.2-m. sorbitol column at 80° demonstrated the presence of 0.37 mole of cyclohexanol (b.p. 160° (742 mm.)) and 0.03 mole of unreacted cyclohexanone. When the sodium methoxide was increased to 3.00 g. (5.55×10^{-2} mole) only 0.0080 mole (2%) of hydrogen gas was evolved as measured by a wet-test meter. The presence of 0.39 mole of cyclohexanol was confirmed by v.p.c. With a 10% excess of sodium borohydride, the reaction mixture contained less than 0.5% of cyclohexanone.

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(17) H. C. Brown, E. J. Mead and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 5400 (1957).

(18) H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3616 (1956).

(19) F. Daniels, J. H. Mathews, J. W. Williams, P. Bender, G. W. Murphy and R. A. Alberty, "Experimental Physical Chemistry," Fourth Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 157–160.

In another series of experiments without methoxide, the addition of solid sodium borohydride (0.100 mole) to 0.400 mole of cyclohexanone in 200 ml. of methanol produced 0.08 mole (20%) of hydrogen while the addition of cyclohexanone to sodium borohydride in methanol produced 0.32 mole of hydrogen gas.

In one series of experiments cyclohexanone (0.400 mole) in methanol was added very slowly to a well-stirred solution of sodium borohydride (0.100 mole) containing methoxide (0.010 *M*). The products were 0.102 mole of cyclohexanol with 0.291 mole of unreacted cyclohexanone and 0.30 mole of hydrogen gas.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, CANADA]

Trifluoromethyl Compounds of Germanium[1]

BY H. C. CLARK AND C. J. WILLIS[2]

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The interaction of trifluoroiodomethane with germanium(II) iodide or stannous iodide has been examined. Trifluoromethyl-tin derivatives are not obtained, but with germanium(II) iodide, *trifluoromethyltriiodogermane* is formed, together with a trace of *bis-(trifluoromethyl)-diiodogermane.* Trifluoromethyltri-iodogermane has been converted to the corresponding trichloro- and trifluorogermane by reaction with the appropriate silver halide. The thermal and hydrolytic stabilities of the trifluoromethyltrihalogermanes have been investigated. With aqueous potassium fluoride, trifluoromethyltrifluorogermane gives the interesting complex, *potassium trifluoromethyl-pentafluorogermanate*, $K_2CF_3GeF_5$.

Organic derivatives of the group IV elements (Si, Ge, Sn and Pb) have been known for many years but until very recently none of their perfluoroalkyl derivatives had been reported. In alkyl or aryl compounds of the type R_4M the reactivity of the M–carbon bond increases greatly along the series M = Si, Ge, Sn, Pb. It is not surprising, therefore, that, while ultraviolet irradiation of a mixture of tetramethyllead and pentafluoroiodoethane is reported to give trimethylpentafluoroethyllead,[3] similar reactions with tetramethyltin are not successful. An alternative route to trimethyltrifluoromethyltin has been found in the reaction of hexamethylditin with trifluoroiodomethane[4]

$$(CH_3)_3Sn\text{–}Sn(CH_3)_3 + CF_3I \longrightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI$$

The success of this reaction, which proceeds under ultraviolet irradiation in excess trifluoroiodomethane as solvent, depends on the ease with which the tin–tin bond is broken. Germanium–germanium and silicon–silicon bonds are much more stable, and we have found that hexamethyldigermane and hexamethyldisilane do not react with trifluoroiodomethane under conditions where hexamethylditin reacted in good yield. In order to extend to germanium our studies on perfluoroalkyl derivatives of the group IV elements, it was therefore necessary to devise an alternative approach to the synthesis of the trifluoromethylgermanium compounds, and to this end use has been made of the strong reducing power of the germanium(II) halides.

Experimental

Volatile compounds were manipulated in a conventional vacuum system and purified by trap-to-trap distillation. Molecular weights were determined by Regnault's method.

Reaction of Germanium(II) Iodide with Trifluoroiodomethane.—Germanium(II) iodide was made from germanium(II) hydroxide and hydriodic acid according to Powell and Brewer.[5] Trifluoroiodomethane (112 g., 0.57 mole, a redistilled commercial sample) was condensed onto germanium(II) iodide (59.7 g., 0.183 mole) in a stainless steel autoclave (300 ml.). The autoclave was heated to 130–135° for 10 days and the volatile products then fractionated to give unreacted trifluoroiodomethane (84.2 g., 0.43 mole) and a small amount (0.3 g.) of a colorless liquid having a vapor pressure of about 2 cm. at 25°. Analysis identified this material as slightly impure *bis-(trifluoromethyl)-diiodogermane.*

Anal. Calcd. for $(CF_3)_2GeI_2$: CF_3, 29.7; I, 54.7; mol. wt., 465. Found: CF_3, 27.8; I, 54.2; mol. wt., 434.

Infrared absorption bands (vapor) were present at 1259 (vw), 1227 (vw), 1167 (s), 1148 (vs), 1119 (w), 1030 (w), 1035 (w), 822 (vw) and 730 (w) cm.$^{-1}$. A yellow oil remaining in the autoclave was removed from unreacted germanium(II) iodide by heating under low pressure and then redistilled *in vacuo* to give *trifluoromethyltri-iodogermane* (40 g., 0.078 mole, distillation temperature 40–42° (10^{-3} mm.), vapor pressure at ambient temperatures 0.2–0.5 mm.).

Anal. Calcd. for CF_3GeI_3: CF_3, 13.2; I, 72.9. Found: CF_3, 12.8; I, 72.8, 72.5.

The compound had f.p. 8.4° and $n^{20}D$ 1.6571. Infrared absorption bands (liquid film) were present at 2240 (vw), 1253 (vw), 1126 (vs), 1038 (w) and 729 (m) cm.$^{-1}$. In the vapor phase, only low pressures were possible because of the low volatility of the compound, and absorption bands were seen at 1165 and 1143 cm.$^{-1}$.

Pyrolysis.—Trifluoromethyltri-iodogermane (3.82 g.) in an evacuated silica tube (15 ml.) was heated to 150° for 48 hr., without any change in appearance. After heating to 180° for 3 days some decomposition was apparent and fractionation of the volatile products gave two fractions; the first (0.154 g.) was shown by infrared spectroscopic examination to be mainly perfluorocyclopropane, with some perfluorocyclobutane and fluoro-olefins, while the second (0.120 g.) was shown to be a mixture of germanium tetrafluoride and tetrafluoroethylene, with a trace of silicon tetrafluoride. After removal of unchanged trifluoromethyltri-iodogermane the orange crystals remaining were identified as germanium(IV) iodide (found, m.p. 143°; lit. m.p. 144°). Thus, approximately 40% of the trifluoromethyltri-iodogermane had decomposed under the conditions used.

Trifluoromethyltrichlorogermane.—Trifluoromethyltri-iodogermane (6.75 g.) was added to carefully dried silver chloride (21.1 g.) in a tube cooled to −196°. The tube was evacuated, sealed and allowed to warm to 20°, when a vigorous reaction occurred. After being kept at 20° for 48 hr. the tube was opened and volatile products were removed

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[3] H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. and Ind.*, 1409 (1959).

[4] H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

[5] H. M. Powell and F. M. Brewer, *J. Chem. Soc.*, 197 (1938).