are probably about 100 times greater for the same brightness value.) While the elimination of sulfate ion from the flux makes the heating time less critical, erratic results were still obtained when different strontium selenide preparations were used. An example of this is given in Table V where results are given for two series of mixtures 100SrSe + XSrO(0.023Sm,0.020Eu)(5LiF) prepared from different batches of strontium selenide. The results are very different in some respects but both series show a maximum in brightness at about 3 parts strontium oxide.

TABLE V

EFFECT OF ADDED OXIDE UPON BRIGHTNESS AND PHOSPHORESCENCE OF SrSe+SrO(0.023Sm,0.020Eu)(5LiF)

Series	X(SrO)	Phosphorescence at 30 seconds after excitation	Relative brightness under I. R. stimulation
1	0	Not detectable	470
	1	72	600
	2	560	4470
	3	2490	6510
	4	5300	3420
2	0	500	6000
	1	200	5400
	2	300	7600
	3	400	11400
	4	500	5900

Although most samples of calcium selenide which have been prepared in this Laboratory contain large amounts of oxide, it was found that good infrared-sensitive phosphors could be prepared from them. The only one which has received more than casual attention is 100(CaSe,CaO)(0.020Sm,0.020Eu)(6CaSO$_4$,6CaF$_2$). The stimulation band for this phosphor is shown in Fig. 6. The emission color is yellow-orange, the peak of the emission band being approximately 0.585 micron. From some X-ray studies of selenide phosphors containing calcium we might infer that the calcium ion tends to form a separate phase with oxide.[15]

Acknowledgment.—The authors wish to thank Dr. W. L. Parker for his determination of the stimulation and emission spectra.

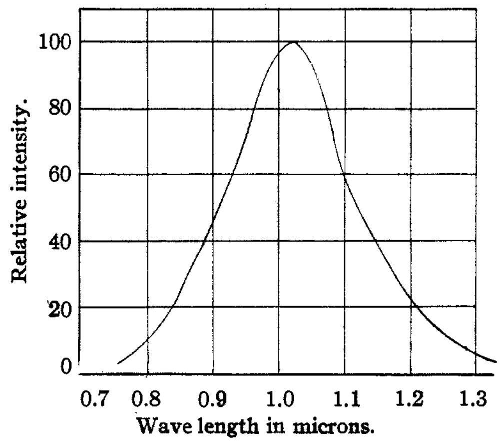

Fig. 6.—Stimulation spectrum of 100(CaSe,CaO)(0.020Sm, 0.020Eu)(6CaSO$_4$,6CaF$_2$).

Summary

A procedure is described for the preparation of strontium selenide suitable for the preparation of infrared-stimulated phosphors.

Several activator pairs are listed which give infrared-stimulated phosphors with strontium selenide. The presence of a small proportion of sulfide or oxide is shown to increase the sensitivity of the SrSe(Sm,Eu) phosphor. Increasing proportions of sulfide cause a shift of the emission color of the phosphor to the red while the oxide in concentrations above 3% causes a rapid decrease in sensitivity.

The emission and stimulation spectra for the 100SrSe + 5SrS(Sm,Eu)(6SrSO$_4$,6CaF$_2$) phosphor and the stimulation spectra for the SrSe(Eu,Bi)-(SrSO$_3$,CaF$_2$) and the (CaSe,CaO)(Sm,Eu)(CaSO$_4$,-CaF$_2$) phosphors are given.

RECEIVED FEBRUARY 11, 1947

[CONTRIBUTION FROM RESEARCH LABORATORY OF GENERAL ELECTRIC COMPANY]

Organic Compounds of Germanium. The Direct Synthesis from Elementary Germanium

BY EUGENE G. ROCHOW[1]

The first organic compound of germanium was prepared by the discoverer of that element, Clemens Winkler,[2] who employed the reaction between zinc diethyl and germanium tetrachloride to make germanium tetraethyl. In the intervening sixty years, many compounds having germanium–carbon linkages have been prepared by further use of zinc alkyls,[3] by the action of sodium on a mixture of germanium tetrahalide and organic halide,[4,5] and by application of the Grignard reaction.[6,7,8] Such methods require the preliminary preparation of an organometallic compound as reagent or rely upon its formation *in situ;* one exception is found in the preparation of ethylgermanium triiodide by the addition of ethyl iodide to germanium diiodide.[9,10]

This paper describes a general method for the preparation of organogermanium halides by the

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[1] Research Laboratory, General Electric Company.

[2] *J. prakt. Chem.*, **144** (N. F. 36) 177 (1887).

[3] Dennis and Hance, THIS JOURNAL, **47**, 370 (1935).

[4] Tabern, Orndorff and Dennis, *ibid.*, **47**, 2039 (1925).

[5] Kraus and Nutting, *ibid.*, **54**, 1622 (1932).

[6] Dennis and Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

[7] Dennis and Patnode, THIS JOURNAL, **52**, 2779 (1930).

[8] Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927).

[9] Flood, *ibid.*, **54**, 1663 (1932).

[10] For a more complete bibliography, see Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937, pp. 295–310.

reaction of alkyl or aryl halides with elementary germanium, preferably in the presence of a metallic catalyst. Perhaps the simplest example is afforded by the reaction of methyl chloride with germanium to form the heretofore unknown dimethylgermanium dichloride and methylgermanium trichloride.

Experimental

Ten grams of massive germanium[11] was crushed in a diamond-point mortar and heated in a current of methyl chloride. No reaction was observed until the temperature reached 460°, whereupon a small amount of liquid product began to condense and carbon began to deposit in the tube. The liquid contained 46% chlorine, which is considerably above the chlorine content of the desired dimethylgermanium dichloride and is further evidence of the loss of methyl groups. In order to introduce a catalyst for the reaction, the germanium was removed from the cooled tube and mixed with an equal weight of reduced copper powder.[12] When this mixture was heated in the stream of methyl chloride, reaction began at only 340° and produced copious quantities of a colorless volatile liquid which behaved like an organogermanium halide.

Further experiment indicated that a smaller proportion of copper catalyst would suffice, so a mixture of 85 g. of powdered germanium and 21 g. of copper was prepared. This was pressed into a disk, broken into lumps and charged in a glass tube sealed to a water condenser and a trap kept at −80°. Methyl chloride was passed through the tube while it was slowly heated. Reaction began at 320° and continued in the range of 320 to 360° for one hundred and ninety hours, after which little germanium remained. One hundred and thirty-two grams of liquid was obtained. Upon fractional distillation, 94 g. was found to boil at 124° and was shown to be dimethylgermanium dichloride, $(CH_3)_2GeCl_2$. In another run, 156 g. of germanium mixed with 31.2 g. of copper and heated in methyl chloride at 320 to 350° for six days yielded 380 g. of liquid product, of which 209 g. was $(CH_3)_2GeCl_2$. This represents 56% of the original germanium; the balance appears as other methylgermanium chlorides and as unreacted germanium.

Analysis.—The fraction boiling at 124.0 ± 0.2° was identified by ultimate analysis. Chlorine was determined acidimetrically on samples hydrolysed in ice water; carbon and hydrogen were determined by microcombustion.[13] Germanium was determined by wet oxidation, but the substance proved difficult to oxidize completely to GeO_2. Drastic oxidation without loss finally was accomplished by an adaptation of the method of Dennis and Hance[3]: the sample was weighed in a vial and the unstoppered vial dropped into 20 cc. of ice-cold fuming nitric acid in a glass-stoppered flask. After the sample had dissolved, 5 g. of ammonium persulfate and 1 cc. of 6 *N* sulfuric acid were added, keeping the flask in an ice-bath. After one hour the flask was allowed to warm and was kept at room temperature overnight. The clear liquid was then transferred to a covered silica crucible and evaporated. The residue was fumed twice with fuming nitric acid, then with sulfuric acid, and finally ignited and weighed as GeO_2. Results were:

	Calcd., %	Found, %			Av.
Ge	41.82	41.07	41.83	42.35	41.75
Cl	40.85	40.84	40.84		40.84
C	13.84	13.85	13.65		13.75
H	3.47	3.37	3.43		3.40
					99.74

The dimethylgermanium dichloride prepared in this manner is a colorless liquid which boils at 124.0°, melts at −22°, has a density of 1.492 at 20° and 1.488 at 26°, and has a refractive index of 1.4552 at 29° for sodium light. It hydrolyses readily in cold water to form a colorless oil which slowly dissolves in 100 volumes of water, a behavior in contrast to the water-repellency of methyl silicone but in accord with the appreciable water solubility of germanium dioxide. If hydrogen sulfide is passed into the acidulated solution, a waxy white solid is precipitated. This precipitate is insoluble in ammonium hydroxide (which dissolves GeS_2) but dissolves in acetone; it is believed to be dimethylgermanium sulfide, $(CH_3)_2GeS$. Hydrolysis of the original dichloride in alkaline 3% hydrogen peroxide fails to oxidize off the methyl groups, for upon acidification to 6*N* with sulfuric acid and treatment with hydrogen sulfide there is precipitated the same white waxy sulfide noted above.

The proportion of dimethylgermanium dichloride in the product from methyl chloride and germanium is surprisingly high when compared with the yield of the corresponding chlorosilane from methyl chloride and silicon under like conditions.[12] Nevertheless, a likely view of the course of the reaction[14] leads one to expect appreciable proportions of the other methylgermanium chlorides. All the distillation fractions containing more than 41% chlorine therefore were refractionated, and there was obtained a small amount of liquid shown to be methylgermanium trichloride, CH_3GeCl_3.

Anal. Calcd.: Cl, 54.83; Ge, 37.43. Found: Cl, 54.33 and 54.33; Ge, 36.9.

The methylgermanium trichloride so obtained boils at 111° and has a density of 1.73 at 24.5°. Further fractionation of the distillates having less than 40% chlorine yielded no recognizable quantity of trimethylgermanium chloride.

To test the applicability of the reaction, a series of experiments with other hydrocarbon halides was undertaken.

A powdered alloy of germanium and copper (in approximately equal proportions) was heated in a stream of ethyl chloride. Reaction began at 320° and produced 5 cc. of liquid which boiled mostly between 144° (the boiling point of $C_2H_5GeCl_3$) and 175° (the boiling point of $(C_2H_5)_2GeCl_2$). The chlorine content was 41.3%, which also lies between that of $C_2H_5GeCl_3$ (51.2%) and that of $(C_2H_5)_2GeCl_2$ (35.2%). These data indicate that the principal product was diethylgermanium dichloride.

Since silver is a more effective catalyst than copper for the direct synthesis of phenylchlorosilanes,[15] a mixture of 80% powdered germanium and 20% silver powder was sintered at 650° and then warmed in a stream of monochlorobenzene. At 440° a reaction took place to form a mixture of phenylgermanium chlorides, and a determination of chlorine indicated that $(C_6H_5)_2GeCl_2$ was the principal product.

A mixture of 10 g. of germanium powder and 10 g. of copper powder was heated in a slow stream of methyl bro-

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[11] Eagle-Picher Co., Joplin, Missouri.

[12] See use of copper as catalyst for the direct reaction of hydrocarbon halides with silicon, THIS JOURNAL, **67**, 963 (1945).

[13] The author is indebted to Lester B. Bronk for the combustion analyses.

[14] Hurd and Rochow, THIS JOURNAL, **67**, 1057 (1945).

[15] Rochow and Gilliam, *ibid.*, **67**, 1772 (1945).

mide. At 340° a reaction occurred, and 28 g. of yellow liquid was obtained over a period of seventy-two hours. The major part of this liquid distilled over the range of 148 to 208°. Trimethylgermanium bromide is the only methylgermanium bromide which has been described,[7] and its boiling point is 113.7°. The reaction product therefore appears to contain dimethylgermanium dibromide and methylgermanium tribromide, and isolation of these new compounds is planned.

From these four examples, it appears that the reaction of hydrocarbon halides with elementary germanium is a general one in which any such halide may react under specific conditions of temperature and catalysis to yield the corresponding organogermanium halides.

Summary

1. A general reaction of hydrocarbon halides with elementary germanium to produce the corresponding organogermanium halides is described.

2. The reaction of methyl chloride with germanium is described in detail to illustrate the effect of metallic copper as a catalyst.

3. The new compounds dimethylgermanium dichloride (b.p. 124°, m. p. −22°, d. 1.492 at 20° and 1.488 at 26°, *n* 1.4552 at 29°) and methylgermanium trichloride (b. p. 111°, d. 1.73 at 24.5°) are described as products of the above reaction.

SCHENECTADY, NEW YORK RECEIVED MARCH 24, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXVIII. Conductance of Some Salts in Nitrobenzene at 25°[1]

BY EDWARD G. TAYLOR[2] AND CHARLES A. KRAUS

I. Introduction

Conductance measurements in ethylene chloride have provided us with much information concerning the influence of specific constitutional factors upon the interactions of ions in a solvent medium of relatively low dielectric constant. Nitrobenzene is a solvent of moderately high dielectric constant, the molecules of which, like those of ethylene chloride, contain no active hydrogen atoms and lack basic properties. Nitrobenzene has a low vapor pressure and is easily obtained in a high state of purity. It is thus suitable for accurate conductance measurements. On account of its relatively high dielectric constant, it has been possible to obtain accurate values for the limiting conductance and dissociation constant of salts which are too weak to permit of accurate evaluation in ethylene chloride. Moreover, a number of salts of inorganic cations are sufficiently soluble to permit of measurement. The dissociation constants of the strongest salts cannot be accurately evaluated because of their almost complete dissociation.

The influence of cationic size on the characteristic constants of electrolytes has been investigated by measurements with a series of homologous tetra-alkylammonium picrates. In order to ascertain the effect of substituting ethyl, hydrogen, hydroxyl, methoxy and phenyl, respectively, for one of the methyl groups in the tetramethylammonium ion, the picrates of ethyltrimethylammonium, trimethylammonium, trimethylhydroxyammonium, trimethylmethoxyammonium and phenyltrimethylammonium have been studied.

Choline picrate and bromomethyltrimethylammonium picrate have been employed to study the effect of replacing an alkyl hydrogen atom by hydroxyl and bromine, respectively. Methoxymethyltrimethylammonium picrate, an isomer of choline picrate, phenyldimethylhydroxyammonium picrate and phenyldimethylammonium picrate have also been investigated.

For the purpose of determining ion conductances, measurements were subsequently carried out by Mr. M. B. Reynolds, of This Laboratory, with tetrabutylammonium triphenylborofluoride. The results of these measurements are included in this paper.

II. Experimental

Apparatus.—Details of the measuring apparatus have been fully described in earlier papers of this series. The conductance cells were of the type described by Cox, Kraus and Fuoss.[3] They were provided with bright platinum electrodes.

Materials.—Nitrobenzene[3a] was fractionally frozen three times, about one-third of the total being poured off as a liquid each time. It was then washed successively with sulfuric acid (1:1), water and sodium hydroxide. The treatment with caustic was continued until the washings were no longer colored. After thoroughly washing with water, the nitrobenzene was dried over calcium chloride. The filtered liquid was fractionated twice under low pressure (<2 mm.). The pale yellow fraction was allowed to stand over powdered barium oxide, filtered and again fractionated (under reduced pressure), this time from activated aluminum oxide. Following the above procedure, solvent having a specific conductance of $2\text{–}4 \times 10^{-10}$ was readily obtained.

The following tetraalkylammonium picrates were prepared and purified by the usual methods: tetramethylammonium picrate, m. p. 318–319°; ethyltrimethylammonium picrate, m. p. 307–308° (dec.); tetraethylam-

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(1) This paper comprises part of the subject matter of a thesis submitted by Edward G. Taylor in partial fulfillment of the requirements for the Degree of Master of Science in the Graduate School of Brown University, May, 1938.

(2) Commonwealth Fellow at Brown University, 1936–1937, 1937–1938. Present address: Williams College, Williamstown, Mass.

(3) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(3a) Oil of Mirbane, kindly donated by the Calco Chemical Company, of Bound Brook, New Jersey.