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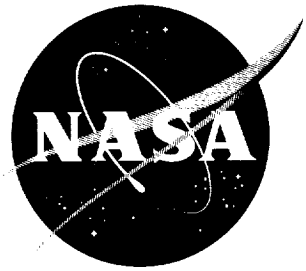

TECHNICAL NOTE
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THE ELECTROCHEMICAL FLUORINATION OF ORGANOSILICON COMPOUNDS

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SUMMARY

The electrochemical fluorination of tetramethylsilane, hexamethyldisiloxane, diethyldichlorosilane, amyltrichlorosilane, and phenyltrichlorosilane was conducted in an Inconel cell equipped with nickel electrodes. A potential of approximately 5.0 volts and a current of approximately 1.0 ampere were used for the electrolysis reaction. In all cases the fluorinations resulted in considerable scission of the carbon-silicon bonds yielding hydrogen and the various fluorinated decomposition products; no fluoroorganosilicon compounds were identified. The main decomposition products were silicon tetrafluoride, the corresponding fluorinated carbon compounds, and the various organofluorosilanes. It is suggested that this is due to the nucleophilic attack of the fluoride ion (or complex fluoride ion) on the carbon-silicon bond.

INTRODUCTION

Electrochemical fluorination of organic compounds (refs. 1 and 2) and alkylsulfur compounds (ref. 3) has produced the corresponding perfluoro compounds in good yields. Therefore, it might be expected that the electrochemical fluorination of organosilicon compounds would likewise yield the perfluoro analogs. Partially fluorinated alkylsilicon compounds have been made by Grignard synthesis (ref. 4) and by photochemical means (ref. 5), while the perfluoroalkylsilicon compounds have been prepared by heating a perfluoroalkyl halide over a mixture of silicon and copper (ref. 6).

It was the intention of this investigation to study the electrochemical fluorination of organosilicon compounds and to determine whether perfluoroorganosilicon compounds could be made by this method. Thus an electrolysis cell similar to that of Simons (refs. 1 and 2) was assembled, and the electrochemical fluorination of tetramethylsilane, hexamethyldisiloxane, diethyldichlorosilane, amyltrichlorosilane, and phenyltrichlorosilane was conducted. The reaction products in all runs were analyzed qualitatively, and in the case of tetramethylsilane and hexamethyldisiloxane the products were determined quantitatively.

APPARATUS

The electrolysis cell was constructed from a $6\frac{1}{2}$-inch length of 3-inch Inconel pipe and contained alternating anode and cathode plates. These electrodes were fabricated from 99.45-percent-pure nickel sheet, 0.032 inch thick, and were spaced 1/8 inch apart with Teflon spacers. During a run the electrodes were immersed to a depth of about $1\frac{3}{4}$ inches in the electrolyte.

The cell was equipped with an inlet tube, a drainage tube, and a reflux tube, all entering the cell through the top. The inlet tube was used for transferring the starting materials into the cell. The drainage tube, which extended to the bottom of the cell, was for removal of nonvolatile liquids from the cell. The reflux tube, which served to condense and return vaporized hydrogen fluoride to the cell, was made from 24 inches of 3/4-inch Inconel tubing and was kept at -30° C by an alcohol-water slush bath.

A line connected to the reflux tube led the exit gases through a dry-ice trap, two liquid-nitrogen traps, and a sulfuric acid bubbler before they were vented to the atmosphere. The bubbler was used to prevent back diffusion of air into the system. A sodium fluoride scrubber could also be connected into the system ahead of the traps for the removal of hydrogen fluoride from the products remaining in the cell after a run. Connected to the traps was a glass vacuum system used for handling the products.

PROCEDURE

For a fluorination run the cell was evacuated and the hydrogen fluoride was condensed in the cell, which was cooled to -78° C. The temperature of the cell was then raised to 0° C and the hydrogen fluoride dried by electrolysis. When the hydrogen fluoride was dry, as noted by a decrease in current, the cell was again cooled (to -78° C) and evacuated of gases. The silicon compound to be fluorinated was then added to the cell, the volatile silicon compounds being let into the cell as gases and then condensed, and the nonvolatile compounds being added as liquids. The cell was then warmed to 0° C, at which temperature the fluorination was conducted. While the cell was warming for the runs in which chlorosilanes were used, a reaction took place between the hydrogen fluoride and the chlorosilanes which gave hydrogen chloride gas and the corresponding fluorosilanes. Since neither the fluorosilanes nor the tetramethylsilane formed a conducting solution with hydrogen fluoride, it was necessary to add sodium fluoride to the cell in these cases.

The fluorination runs were carried out at atmospheric pressure, with an approximate potential of 5.0 volts, a current of approximately 1.0 ampere, and a current density of 0.005 ampere per square centimeter of anode area. The actual conditions employed in each run along with the amounts of starting materials used are given in table I.

Gaseous products obtained during a run were collected in the cold traps and later transferred to the glass vacuum system for analysis. After a run all the liquids in the cell were vaporized, passed through the scrubber to remove hydrogen fluoride, collected in the cold traps, and then transferred to the glass vacuum system to be analyzed. The products of each run were analyzed qualitatively, and the products from runs 1, 2, and 3 were analyzed quantitatively. All the analyses were conducted by infrared methods with pure compounds used as standards.

In several of the fluorination runs made with tetramethylsilane, violent explosions occurred in the liquid-nitrogen-cooled collection traps during the run. It is suspected that these explosions were due to the reaction of hydrogen or methane with fluorine or oxygen bifluoride. Traces of oxygen bifluoride were found in the products, although reasonable attempts had been made to exclude water from the system.

The anhydrous hydrogen fluoride used was obtained commercially and was of 99.9 percent minimum purity. The silicon compounds used were of 97 to 100 percent purity and were further purified by bulb-to-bulb distillation. They were then checked for impurities by infrared analyses and by molecular-weight determinations. No impurities were detected by infrared analysis, and the molecular weights agreed to ±0.1 percent.

RESULTS AND DISCUSSION

The electrochemical fluorination of organosilicon compounds yielded mainly hydrogen and fluorinated decomposition products of the starting material. The decomposition products included silicon tetrafluoride, the various organofluorosilanes, and fluorinated carbon compounds. The major fluorocarbon products obtained in each run are shown in table II and the quantitative analysis of all the products from runs 1, 2, and 3 are shown in table III. In all cases there was considerable scission of the carbon-silicon bonds, with no perfluoroalkylsilanes being identified.

Of the fluorocarbon products of runs 1, 2, and 3, the major product was fluoroform; substantial quantities of carbon tetrafluoride and difluoromethane were also present. In addition to the fluorinated products in runs 1 and 2, considerable amounts of methane were also found. The oxygen in the hexamethyldisiloxane (run 3) apparently had little effect on the fluorination, but rather the silicon-oxygen bond was also cleaved.

The major fluorocarbon products from the fluorination of the alkylsilanes in runs 4 and 5 were the corresponding fluorinated alkane compounds. The fluorination of the phenylsilane in run 6 yielded mostly the perfluorocyclohexane. In addition to the major products, other fluorinated decomposition products were present, which indicated some breaking of the carbon-carbon bonds as well as breaking of the carbon-silicon bonds. These decomposition products were generally present in "trace" amounts. However, in runs 4 and 5 fluoroform and carbon tetrafluoride were present in quantities greater than traces. The unknowns found in runs 5 and 6 showed

considerable absorption in the 7- to 9-micron region of the infrared spectrum which indicated the presence of carbon-fluorine bonds.

It is suggested that the products obtained in this study were the result of nucleophilic attack of the fluoride ion (or complex fluoride ion) on the carbon-silicon bonds subsequent to fluorination of the organo groups. This would agree with statements made in reference 7 on the vulnerability of silicon-halocarbon structures to nucleophilic attack.

CONCLUSION

The electrochemical fluorination of organosilicon compounds resulted in various decomposition products rather than the corresponding fluorinated organosilicon compounds. The decomposition products included silicon tetrafluoride and compounds of the type C_xF_{2x+2}, $C_xF_{2x+1}H$, or cyclo-C_xF_{2x}, the cyclic compound having been formed only when a cyclic starting compound was used.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 12, 1961

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TABLE I. - STARTING MATERIALS

AND CONDITIONS FOR EACH RUN

(a) Starting materials

Starting material	Run					
	1	2	3	4	5	6
	Quantity of starting material, moles					
HF	10.0	9.8	12.5	9.1	15.0	10.3
NaF	.09	.20	-----	.06	.10	.10
$(CH_3)_4Si$	.08	.11	-----	-----	-----	-----
$[(CH_3)_3Si]_2O$	-----	----	.10	-----	-----	-----
$(C_2H_5)_2SiCl_2$	-----	----	-----	.07	-----	-----
$C_5H_{11}SiCl_3$	-----	----	-----	-----	.08	-----
$C_6H_5SiCl_3$	-----	----	-----	-----	-----	.10

(b) Run conditions

Run condition	Run					
	1	2	3	4	5	6
Average voltage	4.9	5.3	5.0	5.0	5.1	5.5
Average current, amp	.9	1.0	1.1	1.0	1.1	1.2
Faradays used	2.59	.70	1.40	2.11	1.63	1.52

TABLE II. - MAJOR FLUOROCARBON PRODUCTS OBTAINED IN EACH RUN

Run	Major fluorocarbon products
1	CHF_3, CF_4, CH_2F_2
2	CHF_3, CH_2F_2, CF_4
3	OF_2, CHF_3, CF_4, CH_2F_2
4	C_2F_6, C_2F_5H
5	C_5F_{12}, unknown (b.p. near 80° C), $C_5F_{11}H$
6	cyclo-C_6F_{12}, unknown (b.p. near 70° C)

TABLE III. - QUANTITATIVE ANALYSIS OF PRODUCTS OBTAINED IN RUNS 1, 2, and 3

Fluorinated products, moles	Run		
	1	2	3
CF_4	0.0172	0.0011	0.0155
CHF_3	.1246	.0169	.0183
CH_2F_2	.0100	.0063	.0047
CH_3F	.0005	.0002	----
C_2F_6	.0046	.0001	.0005
$C_2H_4F_2$	.0061	.0004	----
SiF_4	.0368	.0102	.0088
OF_2	----	----	.0198
$(CH_3)_3SiF$	.0027	.0220	.0961
$(CH_3)_2SiF_2$	.0043	.0076	.0475
$(CH_3)SiF_3$	.0145	.0086	.0167