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ISOTOPIC EXCHANGE OF HYDROGEN BOUND TO SILICON

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This is a part of an extensive investigation in the course of which results have been obtained which may be applied in procedures aiming at the enrichment of heavy hydrogen isotopes. The compounds listed in this paper do not, according to the text, exchange hydrogen under the conditions studied. Consequently, they would hold heavy hydrogen firmly, once it has been introduced by some means other than exchange.

It is known that isotopic exchange of hydrogen atoms at C-H links is strongly retarded or does not take place at all, although it is observed, provided the link is weakened by the proper substitutions in the molecule. This property has been explained (1) as follows: Carbon in compounds is surrounded by an electron shell which contains no free electron pair to which deuterium, from water or another source, can become attached before one of the C-H bonds is broken. Thus the exchange requires a high activation energy and proceeds slowly.

In agreement with these ideas, according to data in literature, the hydrogen exchange is also greatly hampered at H-H and B-H bonds, which also have no free electron pairs.

The same peculiarities must be exhibited by the Si-H bond in organic silicon compounds, where the shell of the silicon atom also does not contain free electron pairs. The study of the isotope exchange in these compounds can serve as further proof of the relationships deduced above, and also is of interest in itself, since it has not yet been investigated.

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In the present work, the exchange of hydrogen at Si-H bonds for deuterium from heavy water and from heavy ethyl alcohol C_2H_5OD was investigated on silanes: $HSi(C_2H_5)_3$ and $HSi(C_6H_5)_3$, and also on triethoxy silane $HSi(OC_2H_5)_3$ under various experimental conditions. These compounds are sufficiently stable in relation to the indicated donors of deuterium.

The initial silicochloroform was obtained by the reaction of HCl on silicon at a temperature of 300° . Triethyl silane is obtained by the reaction of silicochloroform with Grignard reagent and purification by fractionation (bp $107-108^\circ$, $d_4^{20} = 0.7301$). Triphenyl silane is prepared in the same way. The product is distilled off under reduced pressure and solidifies in a colorless crystalline mass at a temperature of 36° . Triethoxy silane is obtained by the reaction of silicochloroform with ethyl alcohol in a benzene solution (2) and is also purified by fractionation (bp 134° , $d_4^{20} = 0.8753$).

The exchange took place in sealed glass ampoules, installed in a thermostat. Water with triethyl silane or triphenyl silane forms a two-phase system, while the former gives a homogenous solution with ethyl alcohol. In several experiments the exchange with water took place in a homogenous pyridine or dioxane solution. Triethoxy silane with ethyl alcohol forms a homogenous solution.

Since the silanes contain a large quantity of nonexchangeable hydrogen atoms for each exchangeable one, the relative change of the density of water is slight even at complete exchange. Therefore, in most of the experiments, the deuterium content of the silane was determined after the exchange. For this purpose, the material was burned and the deuterium content in the water obtained was determined by the flotation method.

Similarly, the deuterium content in ethyl alcohol was determined. In several experiments, the deuterium content in the water was determined after the exchange. In these determinations, no change of density was found which exceeded the limits of experimental error.

The water was separated from the triethyl silane in a separatory funnel. With ethyl alcohol it gives an azeotropic mixture which boils at about 65° . Therefore, after it has been established that there is no exchange with water, the alcohol is washed out by the addition of water. The water is distilled off from triphenyl silane and triethoxy silane with benzene by the procedure of Dean and Stark. Before the isotope analysis, the silanes are cleaned by washing and fractionation.

The results of some typical experiments are given in the appended table, together with the temperature, the time of the exchange, and the catalysts which were added.

From the data given, it can be seen that even under continuous heating with acids or alkalis not one of the three silanes investigated displayed any exchange with heavy water or heavy alcohol. In some cases, a negligible content of deuterium was found. It did not exceed a few percent of that expected in complete exchange. This may be attributed to the inclusion of traces of water.

Analogous carbon compounds displayed similar behavior regarding exchange. Triphenyl methane did not exchange hydrogen with heavy water at 110° for 144 hours in the presence of alkali, isobutane showed only slow exchange with 100 percent pure sulfuric acid containing tritium (3).

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The exchange of hydrogen for deuterium at C-H bonds takes place through ionization or electrophilic substitution (1). The data obtained are insufficient for a comparison of the exchange properties of hydrogen at bonds with carbon and silicon according to the ionization mechanism. The negative electric charge of carbon is greater than that of hydrogen, and this produces a partial polarization of the C-H⁺ bond which favors an electrophilic reaction. On the other hand, the electronegativity of silicon is less than that of the hydrogen, and therefore the bond is polarized in the reverse direction Si⁺-H⁻. In this case, exchange according to the electrophilic mechanism is unlikely and nucleophilic substitution is typical. Accordingly, a nucleophilic reaction takes place between silanes and alkalis, metallic amines, alcoholates, etc.

Until now, the existence of the exchange of hydrogen isotopes by nucleophilic mechanism has not been definitely proved, and the latter is also unlikely because of the low stability of the negative hydrogen ions. It is possible that this explains the absence of exchange in the organic silicon compounds investigated here under the conditions indicated.

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[Appended table follows:]

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Density of Water

<u>Substance</u>	<u>Donor</u>	<u>Catalyst</u>	<u>Temp (°C)</u>	<u>Time (hr)</u>	<u>Initial % of D₂O</u>	<u>From Combustion of Gamma Units</u>	
						(Full ex- change computed)	(Found)
HSi(C ₂ H ₅) ₃	D ₂ O	--	116	51	2.48	165	0
	D ₂ O	H ₂ SO ₄	116	49	2.48	163	0
	D ₂ O	KOH	116	70	2.48	164	4
	D ₂ O+pyridine	--	118	50	20.44	1220	7
	D ₂ O+dioxane	--	100	12	3.25	212	15
	D ₂ O+dioxane	H ₂ SO ₄	100	15	3.25	211	6
	C ₂ H ₅ OD	CH ₃ COONa	116	117	6.49	346	0
C ₂ H ₅ OD	KHSO ₄	118	146	6.49	346	0	
HSi(C ₆ H ₅) ₃	D ₂ O	--	18	335	6.08	306	5
	D ₂ O	--	118	71	2.48	164	7
	D ₂ O	NaOH	103	18	6.04	340	13
	D ₂ O	H ₂ SO ₄	118	70	2.48	165	0
	D ₂ O+dioxane	H ₂ SO ₄	100	15	3.25	212	0
HSi(OC ₂ H ₅) ₃	C ₂ H ₅ OD	--	20	49	6.50	350	2

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