**The First Platinum-Catalyzed Hydrosilylation with Supported Platinum Catalysts**

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The subject of this presentation is the reaction of silicon-hydrogen (Si-H) bonded compounds with unsaturated organics, either C=C or C≡C, using a heterogeneous Pt catalyst. This reaction was first carried out in the Linde Laboratory of Union Carbide and Carbon Corporation at Tonawanda, New York, in 1946. The original patent (US 2,632,013) was filed October 9, 1946. Additional related inventions are disclosed in US Patents 2,637,738; 2,657,114 and 2,851,473.

In 1944, I was moved from the automotive group at Linde to a silicon chemistry group. I was head of the group—five chemists. We were to establish a business based on organosilicon chemicals. The logic was that Union Carbide wanted to expand its chemical business. Already it was a powerhouse in organic chemicals, number two in the nation, DuPont being number one. Several companies had built businesses based on inorganic chemicals. We saw a large undeveloped area in organometallic chemistry. At that time, there were about 92 elements in the Periodic Table. Which metal should we attach organics to? For some time, this small group of five chemists had wandered all over the Periodic Table—chromium, vanadium, and uranium. For various reasons, it was decided that we should stick to silicon. For one thing, it is near carbon in the Periodic Table and should be compatible with it chemically.

Silicon metal was readily available from another division of Union Carbide. But how to attach carbon to silicon, i.e. how do you make a C-Si bond? The Grignard Reaction had been used in universities to do this, but it was too expensive for commercial use. Eugene Rochow, at General Electric Company, had recently discovered and patented the Direct Synthesis method:

$$2CH_3Cl + Si \xrightarrow{\text{Cu}} (CH_3)_2SiCl_2$$
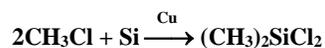
This was a great invention, but it made only a few silicon compounds. While reading, thinking, and studying this problem, one day in early 1946 in the Linde library, it occurred to me like a flash that an SiH bond should react with C=C and C≡C bonds to make Si-C bonds. I talked ideas over with my supervisor, Dr. C. O. Strother. Bond energy calculations indicated that such reactions should be thermodynamically favorable and strongly exothermic. I must have been excited with the idea because I followed the rules to a T: I wrote up an idea record, had it witnessed, and signed it.

I tried the reaction in the lab using a platinum catalyst with the following reactants:

$$Cl_3SiH + CH_2= CH_2 \rightarrow C_2H_5SiCl_3$$

Catalyst = none, reaction Temp. = 350°C.
Catalyst = Pt, Pt on silica Pt on asbestos, reaction Temp. = 100°C.
Olefins: styrene, butadiene, 1-alkenes to octene-1, allylchloride, $CF_2=CH_2$,
vinyl chloride, cyclohexene, trichloroethylene, acetylene,
Other Silanes : $(EtO)_3SiH$, Cl_2SiH_2, $CH_2=CHSiCl_2H$; the latter to oils and
orientable fibers

The reaction was vigorous and complete and occurred at 100°-200°C lower than the uncatalyzed reaction. As indicated above, most of the innumerable C=C and C≡C bonded compounds I tried reacted. By substituting different alkenes for the ethylene, I could change the result from ethyltrichlorosilane to other alkyltrichlorosilanes, and of even greater interest, to organofunctional alkyl chlorosilanes.

By substituting acetylene, I could produce vinyltrichlorosilane. In large scale preparation

$$CH{\equiv}CH(+N_2) + Cl_3SiH \xrightarrow[\text{flow}]{\text{Pt}} CH_2=CHSiCl_3$$

a continuous-flow reactor reduced the subsequent reaction of the product vinyltrichloro-silane with another trichlorosilane to produce $Cl_3SiCH_2CH_2SiCl_3$. An even better method would be a continuous flow over a fixed catalyst bed to avoid $Cl_3SiC_2H_4SiCl_3$.

However, acrylonitrile ($CH_2=CHCN$) was a special case. Its hydrosilylation required a special basic catalyst (as worked out by Dr. V. B. Jex) to give $CNC_2H_2SiCl_3$, which was later converted to either the amino or the carboxy silane. The γ-aminopropyltriethoxy-silane and its analogs were found by one of the glass companies to be the best coupling agent for epoxy resins and were eventually used around the world for this purpose.

$$Cl_2SiH_2 + 2\ CH_2=CH_2 \longrightarrow (C_2H_5)_2SiCl_2\ [T=150°C]$$
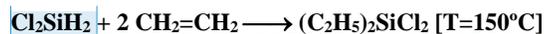
Catalysts: Pt on charcoal (40 m^2/g), on alpha Al_2O_3, on asbestos, on silica gel, or on gamma Al_2O_3 (500 m^2/g).

0.2g gamma Al_2O_3 containing 0.05% Pt (= 0.1 mg Pt) gave 90% conversion of 100 ml SiH_2Cl_2 in 0.8 hr.

As is shown in US 2,851,473 (filed December 23, 1955), platinium on gamma alumina is a superior catalyst for heterogeneous hydrosilylation. In general, the high-surface-area catalysts were best. Note that 0.1 mg of Pt dispersed on gamma Al_2O_3 (~500 m^2/g) gave good conversion in 0.8 hr. It is difficult to imagine a better catalyst. For the

homogeneous catalyst users, it is helpful to remember that silicon oxyhydride, the hydrolyzable product of $SiHCl_3$, is a strong reducing agent. It quickly removes Ag^+ from aqueous solutions as Ag^o. Other SiH hydrolyzates are probably good reducing agents. Aqueous solutions of Pt compounds added to SiH compounds could easily form some metallic Pt.

The extreme activity of Pt-on-γ-alumina catalysts always intrigued me. The usual mechanism of adsorption and desorption of catalyst and product did not seem possible. How could so many molecules adsorb on such a tiny amount of catalyst in such a short time? Yet, the reaction rate increased with the surface area of the catalyst, as an adsorption mechanism would suggest.

My original thought was that the catalyst let loose into the solution free radicals, such as -$SiCl_3$, and subsequent events proceeded by a chain reaction. To test this, we built a pressure reactor with a sapphire head through which ultraviolet light shined continuously. Using trichlorosilane and ethylene, we obtained no reaction. Later Dr. Leo Sommer of Penn. State reacted an alkene (pentene, I believe) with an SiH compound using a peroxide free radical generator and got a very poor yield.

Trichlorosilane is readily prepared from silicon:

$$3HCl + Si \xrightarrow{\text{Cu}} SiHCl_3 + H_2$$
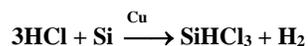
So now we had the basis of an organosilicon business—a way to make a variety of compounds. The heterogeneously catalyzed hydrosilylation reaction was the key to the mission of our small group of Linde researchers, who were funded by Corporation dollars, not Linde's, to find and exploit a route to a business based on organometallics. Initially, there were no uses for the compounds. So two new groups were started at Linde—a research group to find uses for the compounds and an engineering group to learn how to scale up the laboratory operations to plant size. It was an exciting time. We, the research group, converted the Cl-containing compounds to benign liquids, oils, and polymers. This vast group of chemicals was all unknown in nature and new to man. According to Petrov, et al. (Synthesis of Organosilicon Monomers, Consultants Bureau, 1964, p389), the platinum-catalyzed hydrosilylation also provided a new avenue for investigators in the field and greatly expanded synthetic possibilities. The reaction allowed the preparation of a host of previously unknown organosilicon compounds; a new Beilstein was created for these compounds. Union Carbide had faith that uses would be found for them, just as uses were found for other organic fine chemicals when vinyl resins wound up in men's belts, ethylene glycol in auto radiators, etc, etc. These new organosilicon compounds had unusual properties: They were much more resistant to heat than organics, they were not wetted by water, and they had other unusual surface properties. In 1940, sales of these compounds were zero. Today, over $2 billion worth of organosilicon compounds are sold in the USA every year.

Along the way, as part of making new organosilicon compounds, I gained insights into the problem of silicon purification. I studied the chemistry of SiH compounds and learned how to go from $SiHCl_3$ (trichlorosilane) to SiH_4 (monosilane) by a series of so-called disproportionation reactions, such as:

$$SiHCl_3 \longrightarrow SiH_2Cl_2 + SiCl_4$$

$$2SiH_2Cl_2 \longrightarrow SiH_4 + SiCl_4$$
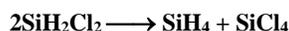
Both of the above happen in sequence, but rapidly. Normally the reactions do not run to completion; all the compounds exist together, in equilibrium. But if you run the reactions in a still and remove the low-boiling compound, they run to completion. Don Bailey and I patented the first reaction.

SiH_4 is a gas that can be purified further by distillation. Pure SiH_4 is easily converted to pure Si by heat:

$$SiH_4 \xrightarrow{\text{heat}} Si + 2H_2$$
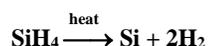
Furthermore, C. E. Erickson and I learned how to recycle the $SiCl_4$ to $SiHCl_3$, which can then be fed back into the beginning of the process:

$$Si + 3SiCl_4 + 2H_2 \longrightarrow 4SiHCl_3$$

We patented this reaction. It consumes metallurgical grade silicon, which is readily available. So the overall process trades impure silicon for pure silicon. Because purifying silicon was incidental to my job of hunting for useful organosilicon compounds, I didn't make a big deal of these discoveries, but I kept Linde informed via internal reports. Much later, Don Bailey put this knowledge to good use when he served as a design consultant for the silicon plant that was built in 1984 in Moses Lake, Washington. Today, that plant makes, by the above reactions, most of the world's premium (99.999999999 percent pure) silicon.

Our work on disproportionation reactions was part of a search for a route to SiH_2Cl_2. This is a difunctional molecule necessary for making R_2SiCl_2, the difunctional monomer needed to make silicone oils and rubber. Our intention was R=ethyl (from ethylene via Pt-catalyzed hydrosilylation), the lowest-carbon-containing silicones available by this route. This would put us in competition with dimethyl silicones, which were the basis for the silicone business of our competitors—Dow-Corning and General Electric.

Much research went into successfully determining how to make oils and rubber out of diethyl silicones. We isolated the cyclic compounds $(Et_2SiO)_x$ from x=3 to 7 and determined their polymerization characteristics. Research was far-ranging. But because of their high-temperature instability relative to the dimethyl silicones, the diethyl silicones were turned down, as a business venture, by the business people in charge of the silicones project at UCC.

All told, I have about 35 US patents related to silicon chemistry. The most important and useful, in my estimation, is that for preparing compounds with silicon-carbon bonds. Making pure Si available to the semiconductor industry by providing chlorosilanes as industrial chemicals was gravy from this. In 1960, I received the Schoellkopf Medal from the American Chemical Society (Western New York Section) for my " pioneering contributions to the technology of polyalkylene oxide lubricants and organosilicon monomers and polymers."

The early books on the history of silicones, one from Dow-Corning and one from General Electric, afforded little space, outside of a footnote, to the heterogeneously-catalyzed, SiH – Olefin reaction. But these authors wrote silicone history from the viewpoints of their laboratories. The full history of silicones at Union Carbide still remains to be told.

Mr. P. W. Shafer and Mr. W. G. Whitehead contributed to the experimental work reported here. Mr. Shafer could build or fix anything mechanical, and Mr. Whitehead always wanted one more experiment for verification.