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Hydrosilylation of Ethylene

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Abstract — Hydrosilylation of ethylene with trialkoxysilanes in the presence of Pt(0) complexes as catalysts affords ethyltrialkoxysilanes in almost quantitative yields. No impurities of vinyltrialkoxysilanes were detected. Experiments and *ab initio* calculations showed that the Pt(0) catalysts are considerably more active in ethylene hydrosilylation than Pt(II) catalysts.

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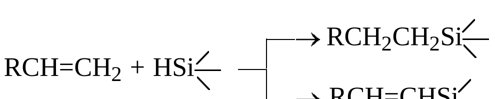
Ethyltriethoxysilane is used for preparing polysiloxanes, organosilicon resins, biologically active substances for agriculture and medicine, etc. Two major synthetic routes to ethyltriethoxysilane are known. The first route is a two-step synthesis: hydrosilylation of ethylene with trichlorosilane followed by etherification of ethyltrichlorosilane with ethanol. The second, more attractive one-step route, hydrosilylation of ethylene and propylene with triethoxysilane, is studied poorly. Hydrosilylation of ethylene and propylene in the presence of a rhodium catalyst, $[RhCl(CO)_2]_2$ (1), was reported [1–5]. However, it is known that the reaction in the presence of rhodium catalysts is accompanied by dehydrogenative hydrosilylation (2) [6].



$$RCH{=}CH_2 + HSi{\lessgtr} \longrightarrow \begin{cases} RCH_2CH_2Si{\lessgtr} & (1) \\ RCH{=}CHSi{\lessgtr} & (2) \end{cases}$$

For example, when the reaction is performed in xylene at 148–225°C, the yield of $EtSi(OEt)_3$ is as low as 28%, whereas the yield of the dehydrogenative hydrosilylation product, $VinSi(OEt)_3$, is 62% [5]. At 20°C, the yield of $EtSi(OEt)_3$ is 95%, but the synthesis takes 65 h. In the presence of the same catalyst, the hydrosilylation of propylene occurs in 3 h at 140–150°C [1].

We believed that it would be more appropriate to look for platinum catalysts for hydrosilylation of ethylene and propylene. First, the side dehydrogenative hydrosilylation is not characteristic of platinum catalysts. Second, platinum catalysts are cheaper than rhodium catalysts. As catalysts we tested Speier's catalyst **I** (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol); carbenium salt **II** $[(Me_2N)_2CCl]_2^+PtCl_6^{2-}$, prepared by us according to [7]; Karstedt's catalyst **III** prepared by us from $H_2PtCl_6 \cdot 6H_2O$ and tetramethyldivinyldisiloxane according to [8] [a complex of Pt(0) with tetramethyldivinyldisiloxane]; catalyst **IV** prepared from hexavinyldisiloxane and $H_2PtCl_6 \cdot 6H_2O$ [9] [a complex of Pt(0) with hexavinyldisiloxane]; and supported catalyst **V** prepared by interaction of Speier's catalyst with porous glass pretreated with diallylaminopropyltriethoxysilane.

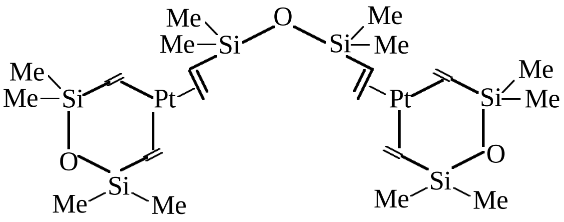
No reaction occurred at 20–100°C in the presence of catalyst **I**. In the presence of catalyst **II**, the reaction did not start at 25–75°C, but at 80–85°C the catalyst instantaneously transformed from a yellow insoluble salt into a brown solution [apparently, a Pt(0) complex]. On this catalyst, ethylene was taken up until the conversion of triethoxysilane was virtually complete. The catalyst appeared to be stable in the presence of ethylene, which suggests its coordination structure. Addition of a new portion of triethoxysilane to the reaction mixture on the next day after the previous run resulted in virtually quantitative reaction, but it was somewhat slower (lower platinum concentration). In the absence of ethylene, a catalytically inactive black precipitate of platinum metal formed on the next day.

In the presence of supported catalyst **V**, which is apparently a complex of platinum with diallylamine immobilized in porous glass, no reaction occurred at 70–80°C, but at 90–100°C ethylene was actively taken up, and the content of ethyltriethoxysilane in the mixture reached 94%. Repeated synthesis on the same

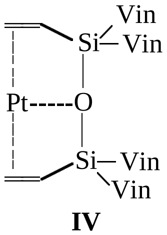
Hydrosilylation of $RCH{=}CH_2$ with trialkoxysilane

R	R'	Amount of $HSi(OR')_3$, ml	Catalyst			Synthesis conditions		Reaction mixture composition, %		
			no.	number of drops (weight, g)	Pt, $C \times 10^3$, %	temperature, °C	time, h	$HSi(OR')_3$	$R''Si(OR')_3$[a]	$Si(OR')_4$
Me	Et	5	**I**	3	7.9	80–100[b]	3	92.5	–	7.5
H	Et	5	**I**	3	7.9	80–100[b]	4	91.5	–	8.5
H	Et	10	**III**	3	11.8	15–53	1/0.5	0	95.3	4.7
H	Et	10	**III**	1	3.93	15–70	1/0.5	0	95.1	4.9
H	Et	20	**III**	1	1.96	17–34[b]	1[c]	–	–	–
H	Et	10	**IV**	1	1.53	23–78	0.7/1	0	95.8	4.2
Me	Et	10	**IV**	1	1.53	23–75	0.6/1	0	95.2	4.8
H	Et	5	**IV**	2	1.53	23–40	1.7/1	0	95.3	4.7
H	Et	4.8	**II**	(0.005)	2.8	23–53	0.5/1	0	95.7	4.3
H	Et	4.8	**II**	[d]	1.4	22–33.5	2/1	0	95.2	4.8
H	Et	2.8	**V**	(0.18)	4.5	70–80	1[c]	–	–	–
H	Et	2.8	**V**	[d]	4.5	90–100	1.5/1	0	94.3	5.7
H	Et	2.8	**V**	[d]	4.5	90–100	2/1	0	94.1	5.9
H	Et	5	**I** + TMDVDS[e]	1 + 1	7.66	18.5–46.5	1/0.5	0	94.9	5.1
H	Et	5	**I** + HVDS[f]	1 + 1	3.06	18–52	2/0.5	0	94.8	5.2
H	Me	2.5	**III**	1	15.32	50–60	2/2	0	75.6	–
H	Me	2.5	**IV**	1	6.12	60–70	1.5/0.5	0	78.8	18.6

[a] $R' = RCH_2CH_2$. [b] With heating. [c] No reaction. [d] Catalyst taken from the previous run. [e], TMDVDS, tetramethyldivinyldisiloxane. [f] HVDS, hexavinyldisiloxane.



III



IV

catalyst was slower, but the conversion of triethoxysilane was complete.

In the presence of catalyst **III**, the reaction started at room temperature 2–5 min after starting the supply of ethylene (or propylene) and was complete in 2.5–3 h. The mixture warmed up to 70°C. In the presence of catalyst **IV**, the reaction occurred similarly (see table).

In virtually all the cases, the starting triethoxysilane reacted completely. The dehydrogenative hydrosilylation product, vinyl- or propenyltriethoxysilane, was never detected (GLC, NMR).

Thus, Pt(0) complexes are active catalysts of hydrosilylation of ethylene and propylene.

Hydrosilylation of ethylene with trimethoxysilane also occurs readily on catalysts **III** and **IV**. The reaction is complete in 1.5–2 h; the content of ethyltrimethoxysilane in the reaction mixture is 66–76%. Dimethylchlorosilane adds to ethylene on these catalysts virtually quantitatively in 1.25–1.5 h; the yield of the adduct in the mixture is 82–87%. Vinyltrimethoxysilane was never detected in the products (see table).

To account for the results obtained, we performed *ab initio* simulation of separate steps of the hydrosilylation on Pt(II) and Pt(0) catalysts. To simplify the calculations, we chose methylsilane as reagent. The approach of methylsilane to a Pt(II) complex (Zeise salt) was simulated in the B3LYP approximation using LanL2MB and LanL2DZ basis sets intended for calculating compounds containing atoms of heavy elements. The results are presented as a plot of the energy of the complex vs. Pt–H interatomic distance (see figure, curve *2*). As the Pt–H distance decreases, the energy of the complex increases. Thus, activation of the Si–H bond along this coordinate does not result in formation of an intermediate compound and is accompanied by a considerable increase in the energy of the system.

To simulate mutual approach of a Pt(0) complex and methylsilane, we used as a model of Karstedt's complex **III** a hypothetical complex of Pt(0) with three ethylene molecules. The calculation results are also presented as a plot of the energy of the system vs. Pt–H interatomic distance (see figure, curve *1*). On the reaction coordinate, there is a minimum corresponding to formation of an intermediate complex with a Pt–H–Si bridging bond.

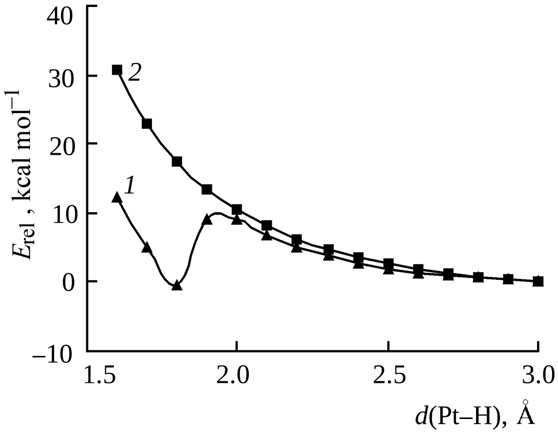
The most stable product of the reaction of the Pt(0) complex is a platinum silicon hydride complex with Pt–H and Pt–Si σ bonds. Calculation of the total potential energy surface of the system corresponding to rearrangement of the complex with a Pt–H–Si bridging bond into a platinum silicon hydride complex with σ bonds shows that the potential barrier of this reaction is low, 15–20 kcal mol^{-1}. Formation of a platinum silicon hydride complex from Pt(II) complexes is not accompanied by formation of structures with Pt–H–Si bridging bonds and requires large energy consumption.

Thus, the Pt(0) complex requires less energy for the activation of the Si–H bond. This fact is apparently responsible for the higher activity of the Pt(0) complex in the hydrosilylation. For the reactions of the Pt(0) and Pt(II) complexes with trichlorosilane, we obtained similar results.

EXPERIMENTAL

The reaction products were analyzed on an LKhM-80 chromatograph equipped with a thermal conductivity detector. The carrier gas was He (30 ml min^{-1}). Stainless steel columns (1000 × 3 mm) were packed with Chromaton N-AW-DMCS (0.25–0.31 mm) + 5% SE-30. The columns were heated from 20 to 300°C at a rate of 16 deg min^{-1}. The vaporizer temperature was 350°C, and the detector temperature, 250°C. The products were identified by GLC using authentic samples.

Ethylene and propylene were not additionally purified. Triethoxysilane was prepared from trichlorosilane; main substance content 91–95%. The compound was distilled before use to obtain 97% pure reagent. Trimethoxysilane was prepared directly from silicon and methanol; the main substance content was 68–80%. The compound was distilled before use to obtain 91% pure reagent.



Energy of complexes of (*1*) Pt(0) and (*2*) Pt(II) with methylsilane as a function of the Pt–H interatomic distance (B3LYP/LanL2DZ).

Hydrosilylation of ethylene. Ethylene or propylene was bubbled through a mixture of hydrosilane and a catalyst. The gas uptake was monitored with Tishchenko bottles filled with polymethylsiloxane liquid and arranged before the device and after the reflux condenser. With an active catalyst, the gas uptake was observed at room temperature (no bubbles appeared in the second Tishchenko bottle after the reflux condenser), and the mixture warmed up. With less active catalysts, the reaction mixture was heated to a temperature at which the gas uptake was observed (50–90°C). After the reaction completion, the mixture was cooled to room temperature and allowed to stand for 1 h, after which the reaction products were analyzed chromatographically.

Catalyst V. To 30 g of porous glass we added 32.5 g of *N*,*N*-diallylaminopropyltriethoxysilane in 150 ml of toluene; the mixture was refluxed for 26 h. Then the glass was filtered off and washed with benzene (20 × 3 ml); excess adsorbate was extracted with hexane in a Soxhlet apparatus for 7 h. The porous glass was filtered off again, washed with ether (10 × 2 ml), and dried in a vacuum for 2 h at 50°C (1 mm Hg). A solution of 2.34 g of hexachloroplatinic acid in 30 ml of isopropyl alcohol was added to the modified glass, and the mixture was allowed to stand for 1.5 months at room temperature. The glass was filtered off, washed with water (30 × 2 ml), alcohol (30 × 3 ml), and ether (30 × 2 ml), and dried first in air and then in a vacuum at 20°C (1 mm Hg) for 8 h. The resulting supported red-brown catalyst **V** contained 0.06% Pt.

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