The hydrosilylation of propylene

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The reactions of separate and competitive hydrosilylation of propylene with $HSiCl_3$, $MeSiHCl_2$, Me_2SiHCl, and $MePh_2SiH$ in the presence of the Speier catalyst (SC) with different additives and a catalyst obtained from SC and propylene were studied. A mutual influence of the hydrosilanes in the competitive reactions was found. The influence of various additives to SC on the process was considered.

Key words: hydrosilylation, propylene, Speier catalyst, catalysis.

The hydrosilylation of propylene is of interest both scientifically and practically. In particular, triethoxypropylsilane and propylsiloxanes are used in the preparation of hydrophobic coatings. Hydrosilylation is the most suitable method for the synthesis of propylsilanes, which is why the choice of an effective catalyst is important for practical use. It is convenient to study hydrosilylation with propylene as an example. First, the hydrosilylation of propylene in the presence of Speiĕr catalyst (SC) proceeds *via* the stage of formation of an intermediate platinum complex with propylene, which is formed in the course of preparation of SC from the Pt^{IV} and isopropyl alcohol. In contrast, with other olefins and speir catalyst (SC) involved in the reaction, the system contains platinum complexes with both propylene and another unsaturated compound added. Second, propylene is also formed in the isomerization reaction that accompanies the hydrosilylation.

Previously,[1–5] we have shown a positive effect of various additives to SC on the hydrosilylation of functionalized unsaturated compounds. In the present work, the effect of some additives was studied by example of hydrosilylation of propylene with trichlorosilane. As can be seen in Fig. 1, the reaction has an induction period in both the presence and absence of additives. Its duration decreases in the series of catalysts: SC + cyclohexanone > SC > SC + mesityl oxide > SC + triethoxyvinylsilane. The reaction rate increases in the reverse order.

The influence of one hydrosilane on the hydrosilylation with another is known from a change in the yield of adducts and hence the activity of silanes in the individual and competitive reactions.[6] The kinetic features of this reaction have not been studied hitherto.

We studied the separate and competitive hydrosilylation of propylene with various hydrosilanes in the presence of SC Freshly prepared solutions of SC were used to exclude the influence of a platinum complex with propylene.

Our experiments showed that the activity of the silanes studied in separate hydrosilylation decreases in the series $MeSiHCl_2$ > $HSiCl_3$ > $MePh_2SiH$ ≫ Me_2SiHCl ≫ $HSi(OEt)_3$ (Fig. 2). The action of triethoxysilane does not initiate hydrosilylation at all.

In the competitive hydrosilylation with the $MeSiHCl_2$—Me_2SiHCl system, the induction period disappears, and the reaction rates come much closer to each other compared to the separate process (Fig. 3, *a*), which suggests that the reaction occurs under the action of one (or essentially one) catalytically active complex. Dichloromethylsilane activates chlorodimethylsilane, while the latter passivates the former.

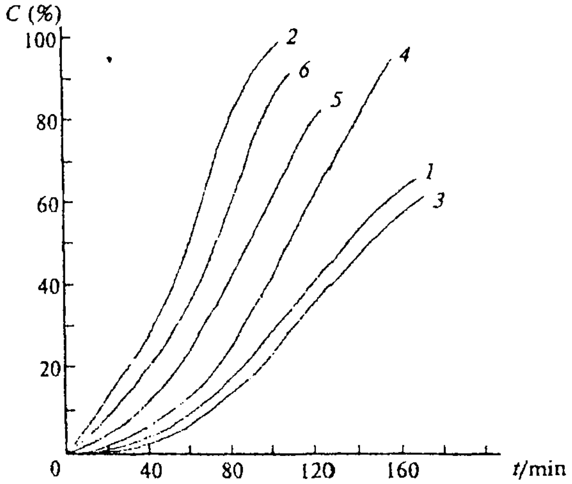


Fig. 1. Hydrosilylation of propylene with trichlorosilane in the presence of (*1*) SC, (*2*) ASC, (*3*) SC with additives of cyclohexanone, (*4*) mesityl oxide, (*5*) triethoxyvinylsilane, and (*6*) chlorodimethylsilane. C (%) is the yield of the adduct.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2048—2051, October, 1998.

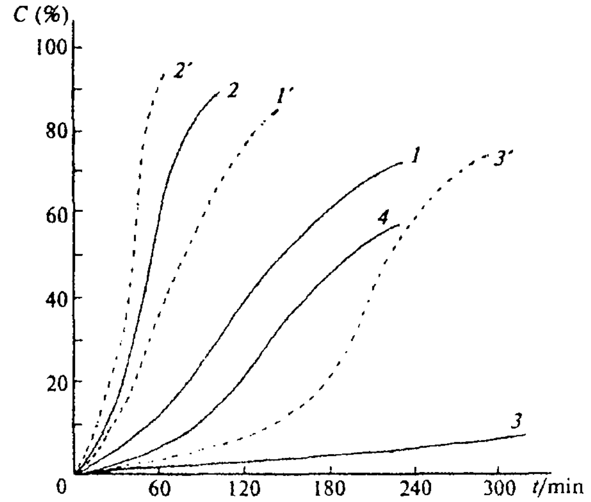


Fig. 2. Hydrosilylation of propylene with (*1,1'*) trichlorosilane, (*2,2'*) dichloromethylsilane, (*3,3'*) chlorodimethylsilane, and (*4,4'*) methyldiphenylsilane in the presence of SC (solid line) and ASC (dotted line).

In the case of the $HSiCl_3$—$MeSiHCl_2$ system, the induction period also disappears, and both the silanes mutually activate each other, but the action of trichlorosilane is stronger, which causes a sharp increase in the formation rate of an adduct with dichloromethylsilane (see Fig. 3, *b*).

When the competitive hydrosilylation is carried out with the $HSiCl_3$—Me_2SiHCl system, the induction period is reduced, and the reaction rates come closer to each other compared to the separate process (see Fig. 3, *c*). These rates were found to be the closest upon addition of SC to chlorodimethylsilane with subsequent addition of trichlorosilane. Both silanes activate each other, trichlorosilane doing it to a larger extent.

The absence of the induction period in our experiments suggests that the hydrosilylation involves platinum silyl complexes. The hydrosilylation of propylene with trichlorosilane and chlorodimethylsilane in the presence of SC and additives of chlorodimethylsilane and trichlorosilane, respectively, occurs similarly to a competitive process, whence one can conclude that intermediate platinum silyl complexes are quite stable and exist over the entire reaction time. Two variants can be supposed, *viz.*, the reaction is catalyzed by a platinum complex containing a nonhydrosilylating silane or a complex with both silanes (or the silyl groups). The second is in better agreement with the reaction rates coming much closer to each other in the competitive hydrosilylation with trichlorosilane and chlorodimethylsilane, when SC was dissolved in the latter with subsequent addition of trichlorosilane. The mutual activating influence of silanes appears in systems whose components differ more strongly in donor-withdrawing properties, *e.g.*, $HSiCl_3$—Me_2SiHCl, $HSiCl_3$—$MePh_2SiH$, but not $MeSiHCl_2$—Me_2SiHCl.

To clear up the role of coordinated propylene, we studied its hydrosilylation in the presence of a platinum propylene complex obtained by alternating repeatedly (3—5 times) evacuation of a vessel containing SC to a residual pressure of 1—2 Torr and its filling with propylene. The obtained solution of a catalyst, which we call "activated Speier catalyst" (ASC), is a yellowish orange liquid well soluble in silanes in an atmosphere of propylene. An analogous procedure with N_2 instead of propylene yielded a dark brown precipitate that is poorly soluble in trichlorosilane with propylene being passed through and similar in activity to SC.

Activated SC appeared to be more active than SC in the hydrosilylation of propylene with trichloro-, dichloromethyl-, and chlorodimethylsilane (see Fig. 2). However, in the case of methyldiphenyl- and triethoxysilanes, platinum metal precipitates, and no hydrosilylation occurs. We found the following order of activity of the silanes in the presence of ASC: $MeSiHCl_2 > HSiCl_3 > Me_2SiHCl$. Thus, ASC can be used in the preparative synthesis of trichloropropyl- and especially chlorodimethylpropylsilanes.

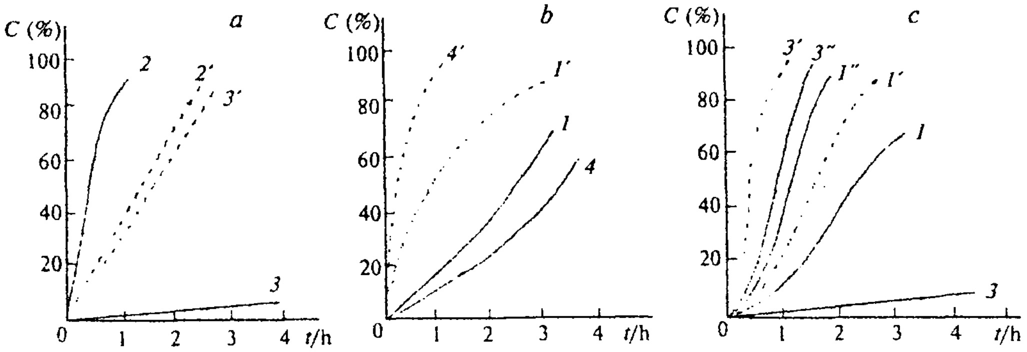


Fig. 3. The separate (solid line) and competitive (dotted line) hydrosilylation of propylene in the presence of SC with the vapors of: (*a*) $MeSiHCl_2$—Me_2SiHCl, (*b*) $HSiCl_3$—$MePh_2SiH$, and (*c*) $HSiCl_3$—Me_2SiHCl. Curves (*1, 1'*) refer to $HSiCl_3$; (*2, 2'*), to $MeSiHCl_2$; (*3, 3'*), to Me_2SiHCl; and (*4, 4'*), to $MePh_2SiH$. Curve (*1"*) refers to the case where SC was dissolved in Me_2SiHCl and added to $HSiCl_3$.

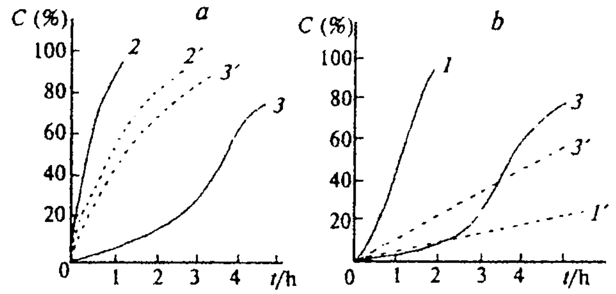


Fig. 4. The separate (solid line) and competitive (dotted line) hydrosilylation of propylene in the presence of ASC with the vapors of: (*a*) $MeSiHCl_2$—$MeSiHCl_2$, (*b*) $HSiCl_3$—Me_2SiHCl; curves (*1,1′*) refer to $HSiCl_3$; (*2,2′*), to $MeSiHCl_2$, and (*3,3′*) to Me_2SiHCl.

In the competitive hydrosilylation with the $MeSiHCl_2$—Me_2SiHCl system in the presence of ASC, as with SC, the induction period disappears, the reaction rates come closer to each other, and dichloromethylsilane activates chlorodimethylsilane, while the latter passivates the former (Fig. 4, *a*).

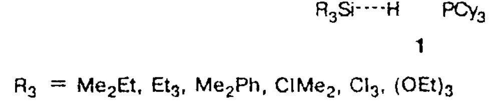
An unexpected result was obtained in the competitive hydrosilylation with the Me_2SiHCl—$HSiCl_3$ system. In the presence of ASC (in contrast to SC), the induction period is absent, and trichlorosilane activates only slightly chlorodimethylsilane, while the latter passivates only slightly the former. The kinetics of the reaction corresponds to the zero order (see Fig. 4, *b*).

The sharp difference in the kinetic curves of the competitive hydrosilylation in the presence of ASC and SC can be explained by the fact that various catalytically active complexes obtained under different conditions are involved in the reaction. Thus, it is known[7] that the presence or absence of an olefin as well as the structure of silane influence the structure of the platinum complex.

Unlike SC that contains $[PtCl_2 \cdot C_3H_6]_2$, ASC obtained in an excess of propylene may be a solution of *cis*-$PtCl_2(C_3H_6)_2$ or a mixture of the complexes in equilibrium:

$$[PtCl_2C_3H_6]_2 + 2\ C_3H_6 \rightleftharpoons 2\ cis\text{-}PtCl_2(C_3H_6)_2. \quad (1)$$

Compounds $(olefin)_2PtCl_2$ are usually colored yellow.[8,9] $[Pt(olefin)_3]$ complexes stable in the presence of excess olefin are also known.[10] It is possible that the interaction of $[Pt(C_3H_6)_2]$ with silanes yields complexes with three-center bonds, similarly to the known reaction of Pt^0 complexes.[11]



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R_3 = Me_2Et, Et_3, Me_2Ph, $ClMe_2$, Cl_3, $(OEt)_3$
Cy — cyclohexyl.

Complexes **1** are more active in hydrosilylation than SC.[12]

ASC is also quite active in the hydrosilylation of other unsaturated compounds. For example, the hydrosilylation of 1,1,1-trifluoropropylene with dichloromethylsilane occurs at room temperature to give dichloromethyl-(3,3,3-trifluoropropyl)silane in 58% yield. When this reaction was carried out under the same conditions in the presence of SC, no adduct was detected.

We showed how the catalyst affects the rate of the hydrosilylation of propylene with trichlorosilane at 20 °C.

Catalyst	$k \cdot 10^{3*}$/min^{-1}
SC	5.33
SC + cyclohexanone	5.10
SC + mesityl oxide	6.22
SC + $CH_2=CHSi(OEt)_3$	8.01
SC + Me_2SiHCl	10.70
ASC	11.40

* The rate constants were determined at a 3—4-fold excess of propylene. The average rate constant values for a 30—60% conversion of silanes are given.

It should be noted that in all of our experiments, only one adduct was detected (GLC data) that corresponds to the addition product according to the Farmer rule.

The hydrosilylation of gaseous olefins is usually carried out either with stirring with a high-speed stirrer or in vessels under pressure. We found a convenient preparative method for carrying out the process in a rotary evaporator, where a large interface can be attained and the liquid phase is continuously renovated. In laboratory, this method can easily yield up to 500 g of the adduct.

Experimental

The products* were analyzed by GLC on an LKhM-80 chromatograph (column 3000×3 mm, Chromaton NEAW+SE-50, helium as the carrier gas (60 mL min^{-1}), detector temperature 250 °C, evaporator temperature 290 °C). The chromatograms were processed with the use of an I-02 integrator. The content of components in a mixture was determined by the internal rating method.

Hydrosilylation of propylene. The synthesis was carried out in a hermetically closed reactor at small gage pressure (0.01 kPa) governed by supplying propylene from a cylinder through a gas preparing block BPG-4. To provide uniform saturation of silanes with propylene, the reactor was equipped with a magnetically driven high-speed (1200 rpm) anchor-type hollow (with vents) stirrer, which allows the reactions to keep the kinetic mode. The reactor was thermostatically controlled at 20±1 °C. The course of the reaction was monitored by periodically performed GLC analyses and recording the volume of the propylene consumed with the use of a gas consumption gage (IRG-110) calibrated for propylene. The consumption values were integrated on the diagram tape of a KSP-4 recorder.

The study of the influence of additive (except for silanes) to SC. The Speier catalyst or SC with an additive was heated at 50 °C for 30 min, cooled, and introduced into the reactor.

The study of the influence of silanes. A silane or a mixture of silanes was added to a freshly prepared SC. After the gas ceased to evolve (5—10 min), the hydrosilylating silane was introduced.

Preparation of ASC. An SC was placed into the reactor. The reactor was filled with propylene, then 3—4 times evacuated to a residual pressure of 1—3 Torr, and re-filled with propylene.

In all cases, **the platinum concentration** was $5 \cdot 10^{-5}$ mol Pt per 1 mol of the olefin.

Hydrosilylation of 1,1,1-trifluoropropylene. Dichloromethylsilane (11.5 g) was added to ASC prepared from 0.1 mL of 0.1 *M* SC. 1,1,1-Trifluoropropylene was supplied, and the reaction mixture was stirred for 3 h. Fractional distillation gave dichloromethyl-(3,3,3-trifluoropropyl)silane (main product content 98.5%). Yield 12.24 g (58%), b.p. 122 °C (756 Torr), d_4^{20} 1.2737, n_D^{20} 1.3840, MR_D 38.77. Calculated: MR_D 38.89 (*cf.* Ref. 13: b.p. 121—122 °C (737 Torr), d_4^{20} 1.2611, n_D^{20} 1.3946).

Hydrosilylation in a rotary evaporator. *A.* Trichlorosilane (1 mol) and 0.1 *M* SC (0.65 mL) were introduced into the flask of a common rotary evaporator. Propylene was added to the rotating flask at room temperature. The consumption of the propylene was completed after 1 h (monitored by rotameter readings). After the catalyst was removed, trichloropropylsilane was obtained (main product content 98.4%). Yield 175 g (98.6%), b.p. 122 °C (750 Torr), n_D^{20} 1.4290 (*cf.* Ref. 14: b.p. 122.2 °C (740 Torr), n_D^{20} 1.4290).

B. The reaction with dichloromethylsilane was performed similarly for 0.5 h. Fractional distillation gave dichloromethylpropylsilane (main product content 98.5%). Yield 141.4 g (90%), b.p. 124.5 °C (750 Torr), n_D^{20} 1.4250 (*cf.* Ref. 15: b.p. 124.4 °C (754 Torr), n_D^{20} 1.4250).

C. Similarly to procedure *A*, dichloromethylsilane (1 mol) and 0.1 *M* SC (1 mL) were introduced into the reactor, and 1,1,1-trifluoropropylene was supplied for 4 h. Fractional distillation gave dichloromethyl-(3,3,3-trifluoropropyl)silane. Yield 116.1 g (55%), b.p. 122 °C (756 Torr), n_D^{20} 1.3840.

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Received December 5, 1997;
in revised form March 5, 1998