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Kinetics and mechanism of the reaction of allyl chloride with trichlorosilane catalyzed by carbon-supported platinum†

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The kinetics of substrate conversions in the commercially important hydrosilylation of allyl chloride with trichlorosilane, catalyzed by active carbon-supported platinum, as well as the yields of the main product (3-chloropropyltrichlorosilane) and by-products (tetrachlorosilane, propyltrichlorosilane) have been studied. On the basis of the measurements performed, the pseudo first-order rate constants (k_{obs}, k_1 and k_2 from the model of competitive reactions) and activation energy ($E_a = 11$ kcal mol^{-1} (46.2 kJ mol^{-1})) were determined. The data obtained point to a non-linear dependence of k_{obs} on the catalyst amount. From the kinetic relationships, the kinetic equation was deduced. All the results of kinetic, IR spectroscopic and thermogravimetric measurements, as well as the derived kinetic equation, have confirmed the general model of consecutive–competitive reaction involving the formation of a surface complex $\mathbf{C_1}$ which can decompose in two directions according to the Chalk–Harrod mechanism. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: hydrosilylation; allyl chloride; trichlorosilane; kinetic equation; Chalk–Harrod mechanism; platinum catalyst

INTRODUCTION

Hydrosilylation of alkenes is one of the most important methods for the synthesis of organosilicon compounds, and is particularly widely used for the production of organofunctional silanes and for cross-linking silicon polymers.[1–4] Although a wide range of catalysts (transition metal (TM) complexes, metals on supports, nucleophiles) have been used for hydrosilylation reactions, most research and industrial syntheses have been carried out in the presence of platinum catalysts or platinum complexes as precursors.[2] Many reviews and original papers have provided an explanation of the mechanism of homogeneous catalysis of hydrosilylation by TM complexes as originally proposed by Chalk and Harrod in 1965.[5] The above mechanism, originally derived from studies of hexachloroplatinic acid as a catalyst precursor, provided a qualitative rational generalization for hydrosilylation activity of other TM complexes. The mechanistic scheme presents conventional oxidative addition–reductive elimination steps to explain how the hydrosilylation occurs. The oxidative addition of trisubstituted silanes to a metal–alkene complex (usually with d^8 or d^{10} configuration) is followed by migratory insertion of alkene into an M—H bond and the resulting metal–(silyl)(alkyl) complex undergoes reductive elimination by Si—C bond formation and regeneration of metal–alkene complex in excess of alkene. Since a facile reductive elimination of silylalkene from alkyl—(M)—SiR_3 species was not well established in a stoichiometric reaction, a modified Chalk–Harrod mechanism was proposed that involves alkene insertion into the metal–silyl bond followed by C—H reductive elimination[4–6,20] (Scheme 1).

Although catalytic cycles of homogeneous TM-catalyzed hydrosilylation processes have been studied in detail since 1965, reports on the kinetic and mechanistic implications of the reactions of catalyzed by metal (platinum) on supports are scarce.[1–3] Colloidal metal formed *in situ* by reduction of

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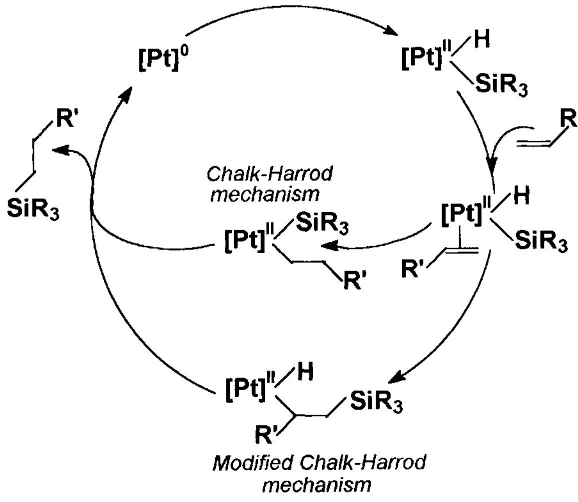


Scheme 1.

metal salts provided a heterogeneous catalyst. Extensive studies, carried out, particularly by Lewis and Stein and their co-workers from General Electric, allowed one to conclude that, regardless of the stoichiometric ratio of hydrosilane to olefin, catalytic hydrosilylation is a molecular process proceeding via metal clusters and that formation of colloids is associated with deactivation of the system.[7,8] Platinum supported on active carbon (usually with a metal loading of 1–5 wt%) is the most frequently used and efficient metal catalyst for commercial hydrosilylation of carbon–carbon multiple bonds, and particularly for the addition of trichlorosilane (TCS) to allyl chloride (AC).[2–4,9,10]

It was reported recently that a heterogeneous catalyst, such as platinum supported on carbon,[11] obtained by treatment of carbon with mesitylene-solvated platinum atoms[12] showed good efficiency in the hydrosilylation of terminal and internal alkynes,[11,12] and bimetallic catalysts (e.g. Pt–Cu) supported on active carbon have been recommended as novel effective catalysts for hydrosilylation of AC, alkenes and fluoroalkenes.[13] A very specific co-activator for Pt/C catalyst appeared to be a peroxide, the continuous presence of which is a means for maintaining high catalytic activity during the reaction.[14]

One of the fundamental reactions involved in the production of silane coupling agents is the addition of TCS to AC, resulting in the formation of 3-chloropropyltrichlorosilane (Cl-PTS), which is a crucial intermediate for production of the whole family of adhesion promoters.[15,16] The process has been commercialized. Therefore, this study is aimed at describing the kinetics and mechanism of the above reaction on Pt/C as used by Degussa–Hülls.

EXPERIMENTAL

Reagents

TCS (>99%) was purchased from Nitrogen Works Ltd, Tarnów (Poland), and distilled under argon prior to use. AC was a commercial product (≥98% purity) subjected to distillation before being used. Pure benzene was used as reaction solvent and *n*-hexane was chosen as a gas chromatography (GC) standard. The catalyst, 1% Pt supported on activated carbon, was obtained from Degussa. Its surface area and pore volume, determined on an ASAP 2010 sorptometer made by Micromeritics, were 1206 m^2 g^{-1} and 0.57 cm^3 g^{-1} respectively. The platinum dispersion, determined on the above instrument, was 33.5%. The FTIR spectroscopic investigation was carried out using a Bruker IFS 113V spectrometer and thermogravimetric analysis (TGA) was performed on an STA 409C 3F instrument made by Netzsch.

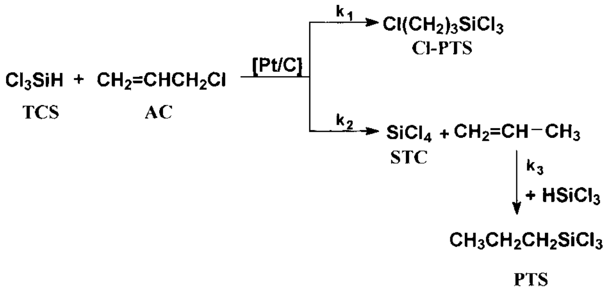
Laboratory setup for kinetic measurements

The reaction vessel (250 cm^3) was equipped with magnetic stirrer, heating system, syringe inlet (for sampling), thermometer, catalyst inlet, and a condenser connected to a cooling system (−25 °C). The condenser was fixed to an absorbing system filled with butanol for entrapping chlorosilanes. The system was opened to allow the discharge of the gas (propene) evolved during the reaction progress. The condenser temperature was controlled by a control unit. The reaction progress was followed by GC analysis, using a Perkin–Elmer Auto System XL gas chromatograph equipped with a 30 m capillary column Megabore (Resteck) DB-1, 1.8 μm, and a TCD detector.

Typical measurement procedure

The substrates, i.e. AC or TCS, solvent and chromatographic standard (hexane) were put into the reaction vessel and warmed up to the desired temperature. After several minutes, the desired amount of catalyst was added via the catalyst inlet and the reaction mixture was intensively stirred at the given temperature. GC analysis of the reaction mixture was performed at the beginning and then every 40 min until conversion of AC (or TCS) exceeded 90%. GC calibration curves were determined for all reagents (the two substrates mentioned above and three products, *viz.* tetrachlorosilane (STC), propyltrichlorosilane (PTS) and Cl-PTS; hence, it was possible to determine the exact molar concentrations of all the reagents in the reaction mixture.

In order to establish the basic conditions for a comprehensive study of the kinetics of the system being discussed, preliminary experiments were carried out to find the effects of the different factors on the yield and selectivity of this complex reaction, namely the effect of solvent, the mode of the substrate and catalyst introduction, and the mixing rate of the reagents and catalyst. The preliminary experiments showed that the reaction proceeds most effectively (in terms of yield and reaction rate) in the absence of solvent, but the kinetic nature of the study forced us to use a solvent. The best choice appeared to be benzene.



Scheme 2.

RESULTS AND DISCUSSION

The complex, competitive–consecutive reaction studied by us proceeds under atmospheric pressure according to Scheme 2.

Kinetic measurements

Kinetic measurements permitted us to determine the pseudo first-order rate constants k_{obs}, calculated from the consumption of substrates (AC and/or $HSiCl_3$). They also allowed us to determine k_1 and k_2, for the formation of Cl-PTS (hydrosilylation product) and STC respectively, from the model of competitive reactions, where $k_{obs} = k_1 + k_2$. The yield of PTS was evaluated simultaneously, which permitted us to calculate k_3. However, some kinetic curves based on the consumption of the substrates do not run to the end; therefore, in such cases, the k_{obs}, calculated from the first-order logarithmic dependence, does not reflect the real observed rate constants. Therefore, the above-mentioned rate constants (k_{obs}, k_1, k_2) were calculated from the initial rates of substrate consumption and the formation of products determined from kinetic curves as an average of all results.

The experiments also enabled us to determine the following optimal condition ranges for kinetic studies. Concentration of substrates: 0.5–5 M (mainly 2 M); optimum ratio of the substrates: [TCS]/[AC] = 1.1–1.3; platinum catalyst to AC ratio: [Pt]/[AC] = 5 × 10^{-5}–10^{-3}; reaction temperature range: 50–70 °C; magnetic stirrer speed: 100–1250 rpm.

Table 1. The effect of the substrate concentrations on the kinetic parameters (in benzene as a solvent)[a]

Concentration (M)				Conversion (%)		10^2 k (min^{-1})		
TCS	AC	TCS/AC	Time (min)	TCS	AC	k_{obs}	k_1	k_2
6.7	2.4	2.8	200	56.2	99.2	2.36	1.71	0.65
2.2	5.8	0.4	200	99.5	33.4	1.62	0.97	0.65
0.6	0.5	1.2	280	84.0	86.5	0.87	0.60	0.27

[a] [Pt]:[AC] = 2 × 10^{-4}, 60 °C, stirring speed 1250 rpm.

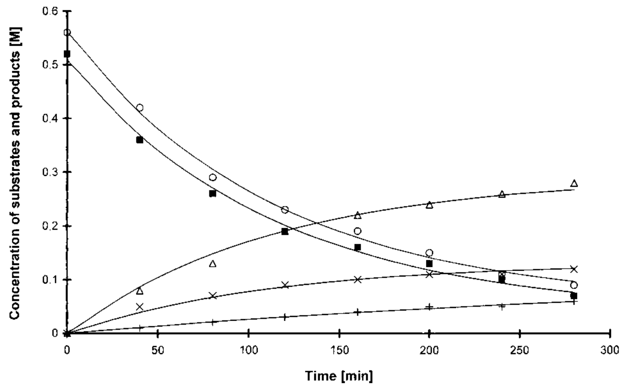


Figure 1. Examples of the kinetic curves: ○, TCS; ■, AC; △, Cl-PTS; +, PTS; ×, STC.

Effect of TCS and AC concentrations and their ratio on the reaction rate

Most experiments were carried in a small excess (1.1–1.2:1.0) of $HSiCl_3$. The excess seems to be necessary because a side reaction (with propene evolution) proceeds in the competitive step of H/Cl exchange in the substrates. However, the order with respect to both substrates was determined on the grounds of experiments performed at 3:1 excess of the particular substrates. Both series of experiments indicate good agreement of the pseudo first-order dependence of the minor substrate uptake. Simultaneously, at equimolar concentrations of both substrates, a pseudo first-order dependence of overall reaction rate constant k_{obs} (calculated from the consumption of substrates) was also found (see Table 1 and examples of kinetic curves given in Fig. 1).

Effect of catalyst amount

This effect was studied under the following conditions: 60 °C, [Pt]/[AC] = 2 × 10^{-4}, 2–3 M of the substrates, [TCS]/[AC] = 1.1–1.3; see Table 2 and Fig. 2.

The curves (Fig. 2) show non-linear dependence of the

Table 2. The effect of the catalyst amount on the kinetic parameters (in benzene as a solvent)[a]

		Conversion (%)		Yield (%)			10^2 k (min^{-1})		
[Pt]/[AC]	Time (min)	TCS	AC	Cl-PTS	PTS	STC	k_{obs}	k_1	k_2
2 × 10^{-5}	320	55.8	61.9	39.6	3.1	13.0	0.26	0.19	0.07
8 × 10^{-5}	280	66.8	74.2	47.1	6.1	13.9	1.10	0.83	0.27
2 × 10^{-4}	240	90.1	89.9	61.6	10.9	17.6	1.68	1.13	0.55
4 × 10^{-4}	200	91.3	91.9	62.1	14.4	15.4	2.86	2.12	0.74
6 × 10^{-4}	80	92.9	93.3	63.1	10.1	18.9	3.24	2.39	0.85
1 × 10^{-3}	120	99.5	96.3	67.1	9.8	21.4	5.31	3.78	1.53

[a] [TCS]:[AC] = 1.2:1, 60 °C, stirring speed 1250 rpm.

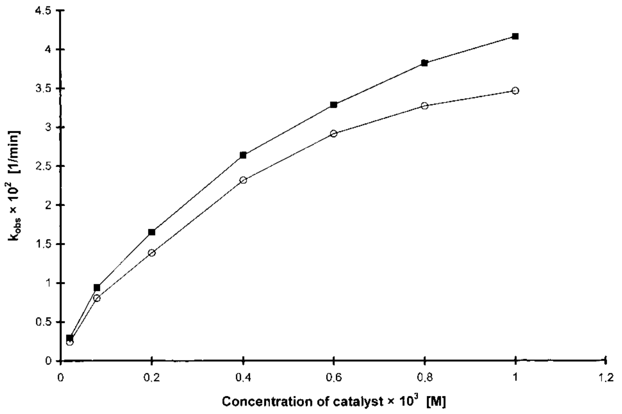


Figure 2. The observed rate constants as a function of catalyst amount: ○, k_{obs} (TCS); ■, k_{obs} (AC).

observed rate constants $k_{obs}^{AC}$and k_{obs}^{TCS}on the catalyst amount. However, all data express a good linear character for the plot of the reciprocal of the observed rate constants $1/k_{obs}$ against the reciprocal of platinum amount 1/[Pt] (see Fig. 3), pointing to a change in the reaction order with respect to catalyst from unity to zero when the concentration of catalytically active sites increases. The physical and mechanistic meanings of this dependence will be discussed later. When plotting the initial rates of the consumption of substrates (k_{obs}[TCS], k_{obs}[AC]) versus the amount of platinum catalyst, we have also observed rather downward deviations from the linear dependence. The rate constants k_{obs}, k_1 and k_2 were recalculated on the basis of preliminary results from all kinetic measurements. In all cases we observed that k_1 was higher than k_2 and it did not depend on the concentration of substrates or the amount of platinum catalyst used (see Tables 1 and 2).

Effect of temperature

We have evaluated the above effect on the basis of data obtained in the temperature range 50–70 °C. When the reaction proceeds at 40 °C, the conversion of the substrates is lower than 60%, but at 80 °C the reaction rate is too high for the methodology accepted to receive reasonable data.

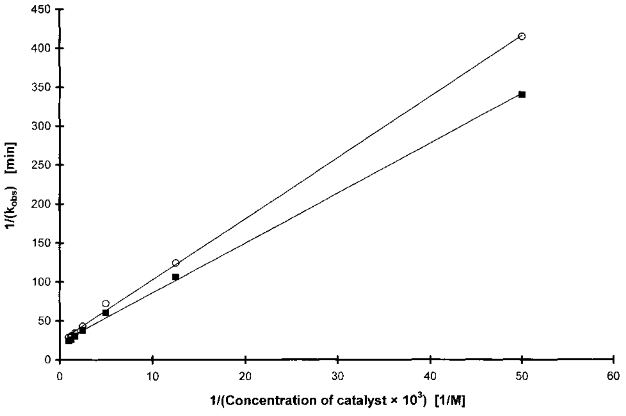


Figure 3. The reciprocal of k_{obs} versus the reciprocal of platinum amount: ○, $1/(k_{obs}$ (TCS)); ■, $1/(k_{obs}$ (AC)).

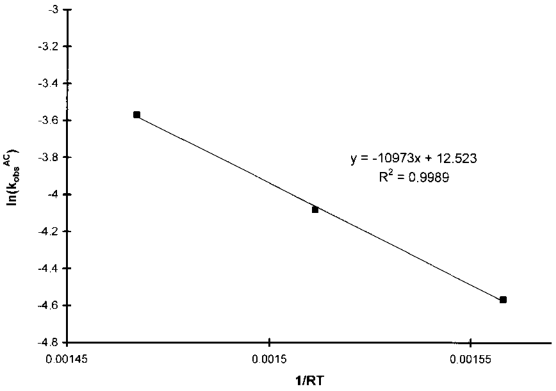


Figure 4. Arrhenius plot.

An Arrhenius plot of the data based on overall k_{obs}^{AC} is given in Fig. 4. The plot allowed us to determine roughly the activation energy E_a, which is equal to 11 kcal mol^{-1} (46.2 kJ mol^{-1}). These results provide a preliminary confirmation of the idea that transport phenomena can play some role in the reactions discussed.

FTIR spectroscopic investigation of Pt/C catalyst

The investigation included recording spectra of the Pt/C catalyst and the catalyst heated in a hydrogen flow at 500 °C, which was followed by heating in the presence of TCS, AC and both parent substances under reflux at 60 °C for 1 h.

Treatment with hydrogen resulted in the appearance of a band at 1726 cm^{-1} (Fig. 5, spectrum 1) and a similar band (shifted to 1733 cm^{-1}) was present in the spectrum of the sample heated in $HSiCl_3$ (Fig. 5, spectrum 2), whereas it was absent in the IR spectrum of the sample heated in AC. The band at 1726 cm^{-1} can also be seen in the spectrum recorded after heating with both $HSiCl_3$ and $CH_2{=}CHCH_2Cl$ (Fig. 5, spectrum 3).

Thermogravimetric measurements

The platinum catalyst surface was flushed with a helium–hydrogen mixture containing 4% H_2 by volume at 500 °C for 1 h in order to remove any chemisorbed oxygen. Then the temperature was lowered to 30 °C and AC or TCS (50 μl) was injected on to the Pt/C catalyst in separate experiments. This was followed by flushing with the above gas mixture at 30 °C for 20 min to get rid of physisorbed adsorbate. Next, it was heated to 400 °C at a rate of 10 °C min^{-1} and the mass loss as a function of temperature was recorded. As is seen in Fig. 6, the courses of the TGA curves of samples loaded with AC and TCS are different. Although in the temperature range up to about 150 °C the TGA curves decline strongly in both cases (as the adsorbates are removed from weaker adsorption

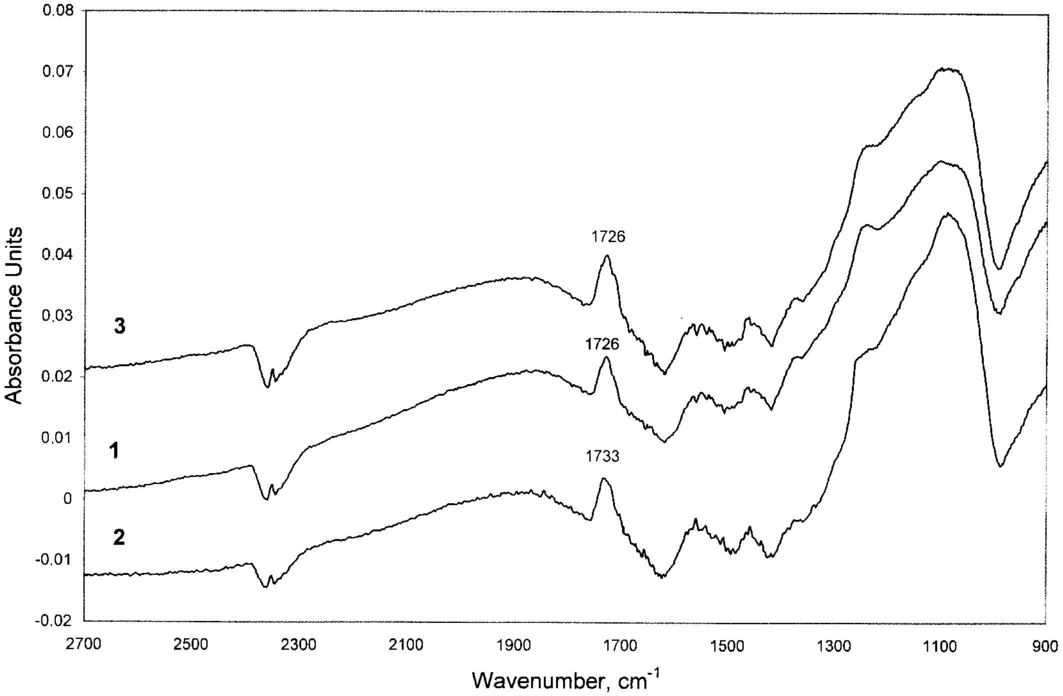


Figure 5. IR spectra of hydrogen-treated Pt/C (1), the above catalyst heated in TCS at 60 °C for 1 h (2), and heated with both TCS and AC at 60 °C for 1 h (3).

centres), later the mass loss recorded for AC stabilizes at an almost constant level, whereas for TCS the TGA curve declines all the time. This points to a strong adsorption of AC, which, after desorption of weakly bound species, remains on the surface even at quite high temperatures. On the other hand, the strength distribution of centres

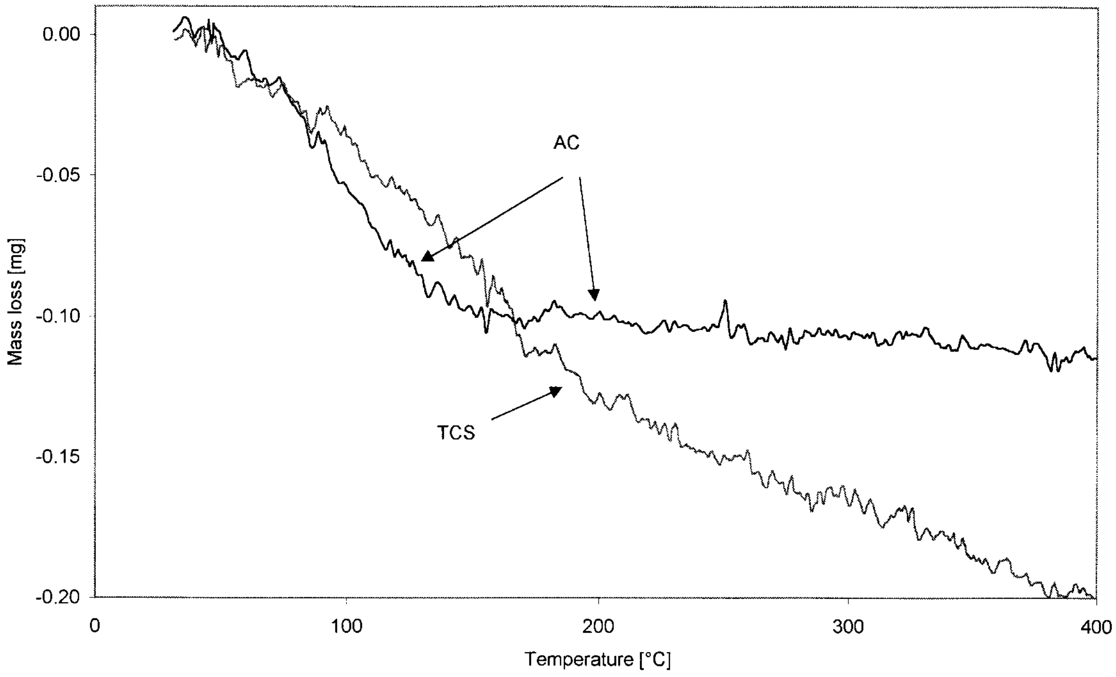


Figure 6. Thermogravimetric curves of the catalyst with adsorbed AC and TCS.

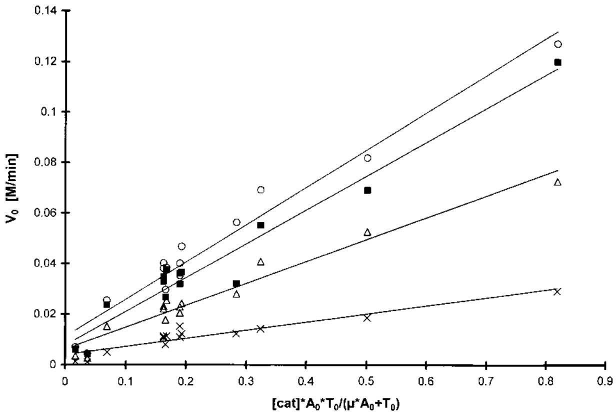


Figure 7. The initial rate as a function of concentrations of the substrates and catalyst: ○, $-V_0$ (TCS); ■, $-V_0$ (AC); △, V_0 (Cl-PTS); ×, V_0 (STC).

capable of adsorbing TCS seems to be very broad, as indicated by the monotonic pattern of mass loss in the temperature range investigated.

MECHANISTIC IMPLICATIONS

The mechanism of this consecutive–competitive reaction was revealed by using kinetic and other physico-chemical methods. On the basis of kinetic measurements, we have formulated a kinetic equation that was derived from the catalytic model. The deduction of the kinetic equation was undertaken by assuming that: (a) quasi-stationary concentrations hold in the case of adsorbed substrates; and (b) desorption of products occurs readily.

The total surface concentration of the catalytically active sites $[\mathrm{Pt}]_0 = [\mathrm{Pt}_{\mathrm{AC}}] + [\mathrm{Pt}_{\mathrm{TCS}}]$, where $[\mathrm{Pt}_{\mathrm{AC}}]$ is the concentration of Pt–AC complex and $[\mathrm{Pt}_{\mathrm{TCS}}]$ is the concentration of Pt–$HSiCl_3$ complex. We can assume that

$$[\mathrm{Pt}_{\mathrm{AC}}]/[\mathrm{Pt}_{\mathrm{TCS}}] = \mu[\mathrm{AC}]/[\mathrm{TCS}] \tag{1}$$

where μ is the affinity factor of the substrates to platinum. After a rearrangement we obtain

$$[\mathrm{Pt}_{\mathrm{TCS}}] = [\mathrm{Pt}_{\mathrm{AC}}][\mathrm{TCS}]/\mu[\mathrm{AC}] \tag{2}$$

and

$$[\mathrm{Pt}_{\mathrm{AC}}] = [\mathrm{Pt}_{\mathrm{TCS}}]\mu[\mathrm{AC}]/[\mathrm{TCS}] \tag{3}$$

After another rearrangement:

$$[\mathrm{Pt}]_0 = \{1 + [\mathrm{TCS}]/\mu[\mathrm{AC}]\}[\mathrm{Pt}_{\mathrm{AC}}] \tag{4}$$

and

$$[\mathrm{Pt}]_0 = \{1 + \mu[\mathrm{AC}]/[\mathrm{TCS}]\}[\mathrm{Pt}_{\mathrm{TCS}}] \tag{5}$$

If we assume that

$$V = -k_{\mathrm{TCS}}[\mathrm{Pt}_{\mathrm{TCS}}][\mathrm{AC}] - k_{\mathrm{AC}}[\mathrm{Pt}_{\mathrm{AC}}][\mathrm{TCS}] \tag{6}$$

$$\begin{aligned} V = {} & -k_{\mathrm{TCS}}[\mathrm{Pt}]_0\{[\mathrm{TCS}][\mathrm{AC}]/(\mu[\mathrm{AC}] + [\mathrm{TCS}])\} \\ & - k_{\mathrm{AC}}[\mathrm{Pt}]_0\{\mu[\mathrm{AC}][\mathrm{TCS}]/(\mu[\mathrm{AC}] + [\mathrm{TCS}])\} \end{aligned} \tag{7}$$

then

$$V = -(k_{\mathrm{TCS}} + \mu k_{\mathrm{AC}})[\mathrm{Pt}]_0[\mathrm{TCS}][\mathrm{AC}]/(\mu[\mathrm{AC}] + [\mathrm{TCS}]) \tag{8}$$

For $t = 0$:

$$V_0 = -(k_{\mathrm{TCS}} + \mu k_{\mathrm{AC}})[\mathrm{Pt}]_0[\mathrm{TCS}]_0[\mathrm{AC}]_0/(\mu[\mathrm{AC}]_0 + [\mathrm{TCS}]_0) \tag{9}$$

Equation (9) was used to plot the initial rate as a function of the concentration of substrates and the amount of catalyst for $t = 0$ (see Fig. 7).

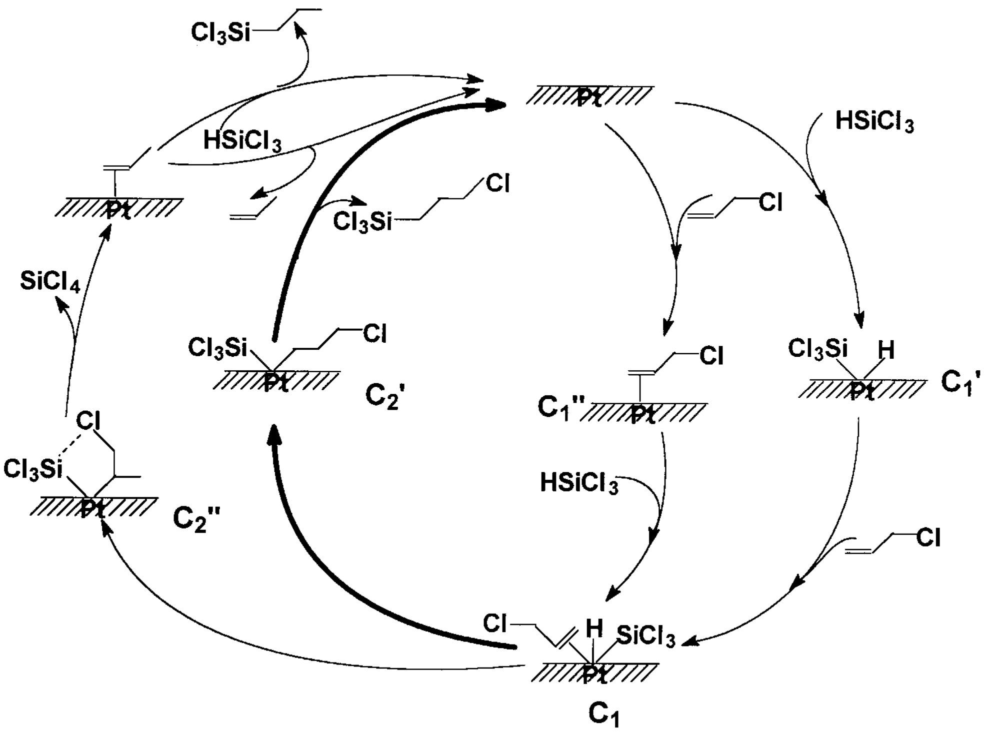
For the linear plot, the following values were found: $k_{\mathrm{TCS}} = 0.0875$; $k_{\mathrm{AC}} = 0.0395$; $\mu = 1.94$.

The results of all the kinetic, FTIR spectroscopic and thermogravimetric measurements confirm the general scheme of the reaction presented in Scheme 2, and this permits us to propose the catalytic cycle of this reaction in Scheme 3.

The band at 1733 cm^{-1} observed in the FTIR spectra of the Pt/C catalyst[17] in contact with TCS provides evidence for oxidative addition of the latter compound.

Thermogravimetric measurements confirm the reversibility of the oxidative addition process of $HSiCl_3$ to platinum on the surface (complex $\mathbf{C'_1}$ in Scheme 3). Contrary to adsorption of $HSiCl_3$, some of the AC is adsorbed irreversibly on platinum atoms present on the surface of the Pt/C catalyst, forming complex $\mathbf{C''_1}$.

In both variants, the key step is the formation of the surface complex $\mathbf{C_1}$, which can be realized by two consecutive steps (adsorption and reaction of both substrates) on the catalytically active sites of the surface. This complex $\mathbf{C_1}$ decomposes in two directions after prior insertion of the olefin into Pt—H to yield the hydrosilylation product or $SiCl_4$ and propene (coordinated to platinum). The latter step can be followed by either consecutive reaction with $HSiCl_3$ to give PTS or propene evolution. The rate-determining step (according to the general model of catalysis of hydrosilylation by transition metals) is the formation of a π–σ complex. Thus, in this heterogeneous system, the formation of the $\mathbf{C_1}$ substrate intermediate (via two different reversible pathways) and its decomposition in two directions seems to be the controlling step in these competitive–consecutive reactions proceeding according to the Chalk–Harrod mechanism. A modified version of this concept (see Scheme 1) was ruled out on the grounds of a recent detailed theoretical study of platinum-catalyzed hydrosilylation of ethylene,[18,19] which concluded that the above process proceeds according to the Chalk–Harrod mechanism. The rate-determining step in this mechanism was the isomerization of the Pt–(silyl)(alkyl) complex formed by ethylene insertion into the Pt—H bond and the activation barrier of this step was 23 kcal mol^{-1}



Scheme 3.

(96.6 kJ mol^{-1}) for R = Me and 26 kcal mol (109.2 kJ mol^{-1}) for R = Cl. However, in the modified Chalk–Harrod mechanism, the rate-determining step was the insertion of ethylene into the Pt—SiR_3 bond, and its activation barrier was 44 kcal mol^{-1} (184.8 kJ mol^{-1}) for R = Me and 60 kcal mol^{-1} (252 kJ mol^{-1}) for R = Cl.

The kinetic data were also confirmed by TGA measurements, which suggest that the adsorption of AC is stronger than that of TCS (by the factor $\mu \approx 2$).

CONCLUSIONS

The results of the experiments performed in this study, of the hydrosilylation of AC with TCS, have permitted us to deduce the kinetic equation derived from the catalytic model by assuming quasi-stationary concentrations of adsorbed substrates and desorption of products.

All kinetic, IR spectroscopic and thermogravimetric measurements, as well as the derived kinetic equation, have confirmed the general scheme of the consecutive–competitive catalytic reaction involving the formation of the surface complex $\mathbf{C_1}$, which can decompose in two directions according to the Chalk–Harrod mechanism.

Acknowledgement

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