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Catalysis of hydrosilylation XIII.* Gas-phase hydrosilylation of acetylene by trichlorosilane on functionalised silica supported rhodium and ruthenium phosphine complexes

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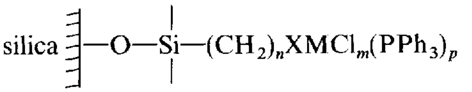
Gas-phase hydrosilylation of acetylene by trichlorosilane catalyzed in a continuous flow apparatus by rhodium and ruthenium phosphine complexes immobilized on the silica via mercapto, phosphine, amine and nitrile ligands has been studied. GLC analysis of the reaction products showed vinyltrichlorosilane to be accompanied by products of double hydrosilylation of acetylene and the redistribution of trichlorosilane followed by the hydrosilylation and hydrogenative hydrosilylation of acetylene with dichlorosilane. A scheme for this complex competitive–consecutive reaction was proposed. The yield and selectivity of vinyltrichlorosilane can be much improved under special reaction conditions, e.g. rate flow of the particular substrates, temperature, given catalyst and others. Kinetic measurements carried out in the range of 115–140°C allowed us to evaluate the activation energy, E_a, for the vinyltrichlorosilane synthesis, which varied between 20.5 and 27.6 kJ mol^{-1} for the selected rhodium and ruthenium supported complexes.

Keywords: Hydrosilylation, acetylene, trichlorosilane, silica, rhodium, ruthenium, catalysis

INTRODUCTION

Vinyl(organo)substituted silanes are fundamental organosilicon monomers also commonly used as important silane coupling agents and reagents in organic synthesis.[1] Therefore, a great interest in industry for new effective catalysts and systems for vinylsilane production is still observed. Various transition metal complexes are well-known catalysts for synthesis of vinyltrisubstituted silanes in the liquid phase.[2,3] On the other hand, platinum heterogeneous and supported complex catalysts are extensively applied in the reaction of trisubstituted silanes with acetylene in the gas phase. In the latter, flow methods or a high-pressure autoclave are employed at elevated temperatures.[4–8] Some, mainly platinum and palladium supported complexes, are also used as catalysts of the reaction occurring in the liquid phase.[9–13] The main purpose for most investigations on acetylene hydrosilylation is to find, under mild conditions, not only active but above all selective catalysts that could eliminate the product of double hydrosilylation, bis(silyl)ethane, as well as redistribution reactions of the initial hydrosilanes.

Our study was aimed at testing rhodium and ruthenium complexes as effective supported catalysts of the given structure (Scheme A)



$$\text{silica}-O-\overset{|}{\underset{|}{Si}}-(CH_2)_nXMCl_m(PPh_3)_p$$

[A]

$M = Rh(I)$, $Ru(II)$: $X = PPh_2$, CN, SH, $NHCH_2CH_2NH_2$, $N(CH_2CH_2)_2O$: $n = 2, 3$: $m = 1, 2$, for the hydrosilylation of acetylene by trichlorosilane proceeding in a flow mciroreactor under normal pressure. In addition, a detailed analysis and identification of the main reaction products and most by-products as well as kinetic and catalytic data would enable us to discuss a catalytic cycle for the reaction examined.

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EXPERIMENTAL

Materials

$RhCl(PPh_3)_3$ was prepared from $RhCl_3 \cdot 3H_2O$ according to a well-known method. The solvents were dried and, as with trichlorosilane, redistilled prior to use. Acetylene was purged using several gas washing bottles including solutions of Cr_2O_3 in H_2SO_4, $HgCl_2$ in HCl, $Cu(NO_3)_2$ in HNO_3 and 30% KOH as well as dry KOH. 3-Chloropropyltrichlorosilane and 2-cyanoethyltrichlorosilane were prepared by the addition of trichlorosilane to 3-chloro-1-propene and 2-cyano-1-ethene, respectively in the presence of homogeneous platinum[12] and ruthenium[14] complexes. 3-Chloropropyltriethoxysilane and 2-cyanoethyltriethoxysilane were obtained by the alcoholysis of the respective chlorosilanes. 3-Mercaptopropyltriethoxysilane (Union Carbide) and N-2-aminoethyl-3-aminopropyltriethoxysilane (Dow Corning) were commercial products used as received. Triethoxysilylpropyldiphenylphosphine was obtained by treating 3-chloropropyltriethoxysilane with $LiPPh_2$ in THF according to a given method.[15] $(C_2H_5O)_3Si(CH_2)_3N(C_2H_4)_2O$ was prepared by the reaction of 3-chloropropyltriethoxysilane with morpholine.[16]

Preparation of supports

Support S_A

10 g of degassed and dried silica gel (Lichrosorb 100, Merck) were added to 6 cm^3 $(C_2H_5O)_3SiCH_2CH_2CH_2PPh_2$ and 30 cm^3 of dry benzene. The mixture was refluxed for 24 h with continuous stirring. After the completion of the reaction the solid was filtered off, extracted and washed with benzene in a Soxhlet apparatus and dried in vacuo.

Supports S_B and S_G

56 g of silica (MN-Kieselgel-60) were added to 15 cm^3 of $(CH_3O)_3SiCH_2CH_2CH_2SH$ and 300 cm^3 of benzene. The mixture was refluxed for 14 h. The silica was then filtered off washed and dried in vacuo. After drying the modified silica was treated with hexamethyldisilazane for 12 h in order to block the remaining silanol groups.

Support S_C

30 g of silica (MN-Kieselgel-60), 14 cm^3 of $(C_2H_5O)_3SiCH_2CH_2CN$ and 150 cm^3 of benzene were refluxed for 14 h and subsequently this modified silica was treated according to the procedure given for the support S_B.

Supports S_D and S_H

80 g of silica (MN-Kieselgel-60), 20 cm^3 of $(C_2H_5O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$ and 350 cm^3 of benzene were refluxed and subsequently this modified silica was treated according to the procedure given for the support S_B.

Support S_E

15 cm^3 of $(C_2H_5O)_3SiCH_2CH_2CH_2N(CH_2CH_2)_2O$ dissolved in 50 cm^3 of benzene was added to 40 g of silica (Kieselgel 100–200 mesh, International Enzymes Ltd) and then treated as given previously.[16]

Support S_F

The preparation of this support was based on the method of Allum et al.[17] and was carried out using 40 g silica (Kieselgel 100–200 mesh, International Enzymes Ltd) and 20 cm^3 of 3-chloropropyltriethoxysilane in benzene solution (100 cm^3). A solution of lithium diphenylphosphine in THF was added to the modified silica (25 g) and treated according to the method given earlier.[17]

Preparation of catalysts

$RhCl(PPh_3)_3$ (1 g) or $RuCl_2(PPh_3)_3$ (0.5 g) was dissolved in chloroform (catalyst A) or in benzene (catalysts B–H) (100 cm^3) and the solution was added to the modified supports (5 g of S_A–S_H). The mixture was then stirred at room temperature under dry argon for 10 h, extracted with chloroform (catalyst A) or benzene (catalysts B–H) for 6 h in a Soxhlet apparatus (also under argon) and dried in vacuo for 24 h. This resulted in our obtaining supported catalysts of rhodium A, B, C, D, E and ruthenium F, G, H. Elemental analyses of the supports as well as the metal content in the catalysts are presented in Table 1.

Procedure and apparatus

Most of the catalytic experiments in the gas-phase hydrosilylation of acetylene were carried out in a continuous flow apparatus (Fig. 1) equipped with a microreactor (D) made of Pyrex glass (15 mm diameter, 120 mm long), a gas purification system (A), gas flow control system (B) and with gas chromatographic analysis for the

Table 1 Elemental analysis of the silica supports S_A–S_H and of the metals in catalysts of the general formula $\rbrack$—O—Si(CH$_2$)$_n$XMCl$_m$(PPh$_3$)$_p$, M = Rh(I), Ru(II), X = anchored ligand

Support				[%]								
S	n	$-X$	Catalyst	C	H	P	N	S	Cl	Rh	Ru	$[X]/[M]$
S_A	3	—PPh$_2$	A	8.74	1.18	1.60	—	—	—	1.3	—	4.1
S_B	3	—SH	B	4.33	1.08	—	—	2.36	—	1.1	—	6.9
S_C	2	—CN	C	3.70	0.80	—	0.68	—	—	0.35	—	14.3
S_D	3	—NHCH$_2$CH$_2$NH$_2$	D	5.87	1.36	—	2.33	—	—	0.8	—	10.7
S_E	3	—N(CH$_2$CH$_2$)$_2$O	E	4.55	0.98	—	0.69	—	—	0.8	—	6.3
S_F	3	—PPh$_2$	F	10.10	1.58	2.65	—	—	1.34	—	1.0	8.6
S_G	3	—SH	G	4.33	1.08	—	—	2.36	—	—	1.1	6.8
S_H	3	—NHCH$_2$CH$_2$NH$_2$	H	5.88	1.36	—	2.33	—	—	—	1.0	8.4

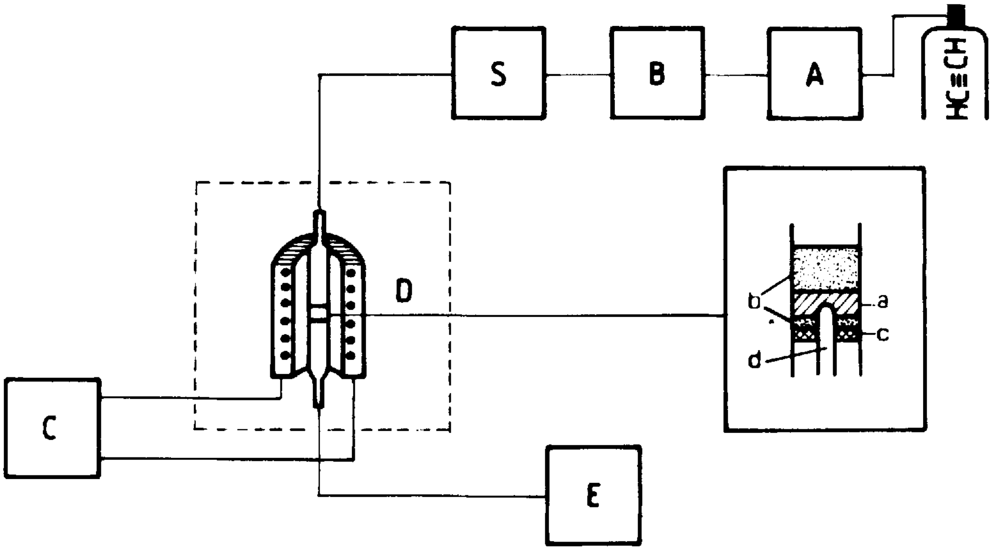


Figure 1 Scheme of apparatus for catalytic experiments: A–gas purification system, B–gas flow control system, C–microreactor temperature control system, D–microreactor system, E GLC system, S–gas sampling system, a–catalyst, b–glass beads, c–glass wool, d–thermocouple pocket.

reaction mixture (E). A mixture of the purified acetylene and hydrosilane was sampled (S) with given flow rate (0.3–1 dcm^3 h^{-1}). The process was carried out in the temperature range 80–170°C. The catalyst (0.2–0.6 g) was placed in the microreactor on glass wool and was covered by glass beads. The reactor was heated electrically and a thermostated heater was used, permitting isothermal operation to within ± 0.5°C. The catalyst was activated in an acetylene flow at 120°C for 1.5 h. Repeatable data for the hydrosilane conversion, the yield and selectivities of the products as well as the rates of the hydrosilylation process was obtained after a one hour reaction period. The ranges of flow rates essentially were 1.7–8.8 mmole (HSiCl$_3$) h^{-1} and 18–45 mmole(C$_2$H$_2$) h^{-1}.

The reaction mixture was periodically analyzed by a gas-chromatograph (GChF 18.3, GDR) equipped with a thermal conductivity detector. Hydrogen as carrier gas and 10% SE-30 on Chromosorb P-AW-DMCS column (3 m × 0.4 cm) were used. The microreactor was directly attached to the chromatograph through a 6-way valve. Vinylsilane as the main product and other by-products were recorded by GLC. The products obtained were identified by comparison of their retention times with those of authentic samples. The selectivity S_1 for the formation of vinylsilane was calculated as follows (Eqn 1):

$$S_1 = \frac{a_1}{a_1 + a_2 + \cdots + a_n} \, [\%] \qquad [1]$$

where $a_1, \ldots, a_n$ are the integrated peak areas for vinylsilane (a_1) and by-products. The selectivities $S_2, \ldots, S_n$ were calculated by the same method. The yield of the vinylsilane was evaluated from the following equation (Eqn 2):

$$Y_1 = \frac{S_1 \cdot C_H}{100} \, [\%] \qquad [2]$$

where C_H—conversion of hydrosilane [%],
S_1—selectivity for vinylsilane [%].

The reactor was operated differentially, so that the initial rate of hydrosilylation could be expressed[18] as Eqn 3:

$$r = \frac{Y_1}{100 \cdot W/f} \left[\frac{\mathrm{cm}^3}{\mathrm{g \cdot s}}\right] \qquad [3]$$

where W—the weight of catalyst used [g],
f —the flow rate of hydrosilane [$\mathrm{cm}^3\,\mathrm{s}^{-1}$],
r —expressed in cm^3 vinylsilane (at 0.1 MPa and 20°C) per gram of metal and per second.

RESULTS AND DISCUSSION

The prepared supported catalysts of rhodium (A–E) and ruthenium (F–H) were used in the gas-phase hydrosilylation of acetylene by trichlorosilane. In this reaction the following products and by-products were detected (GLC) and identified: vinyltrichlorosilane (1), 1,2-bis(trichlorosilyl)-ethane (2), $SiCl_4$ (3) and $C_2H_5SiCl_3$ (4). Traces of other unidentified by-products (5) (mainly redistribution products) were also recorded under some conditions, especially in the presence of ruthenium catalysts and on fresh catalysts. An example of a gas-chromatogram record is given in Fig. 2A. The presence of H_2SiCl_2 as a product of redistribution of the trichlorosilane was noted by GLC in the separate experiment carried out in the absence of acetylene (Fig. 2B).

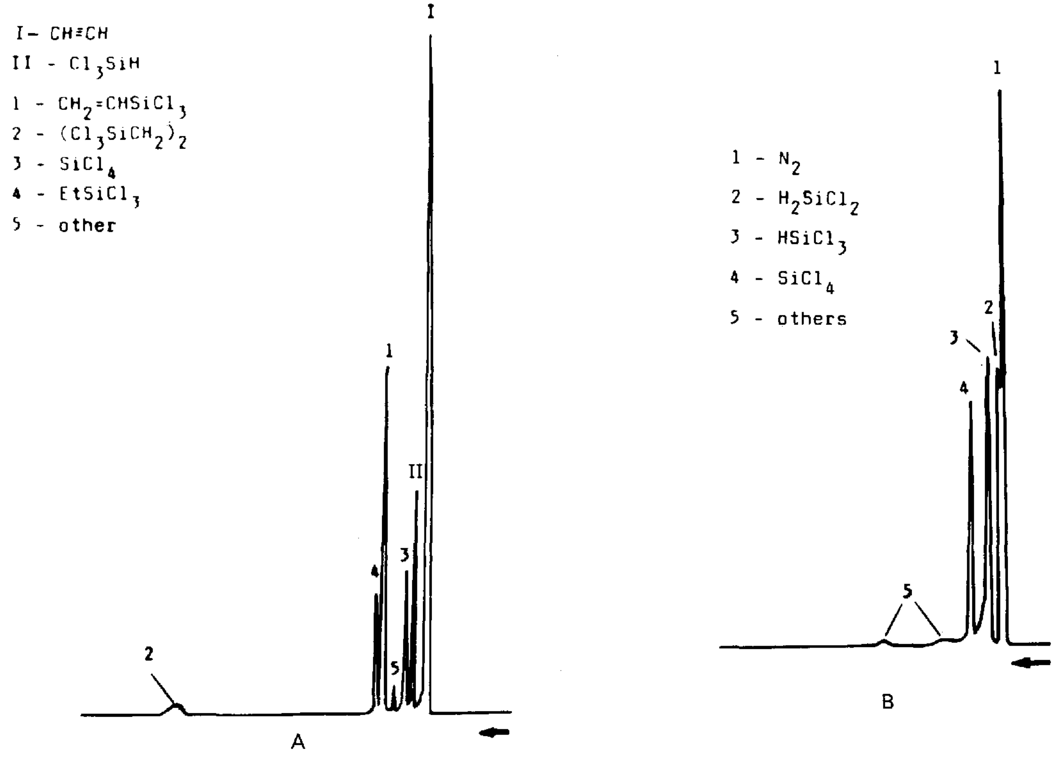


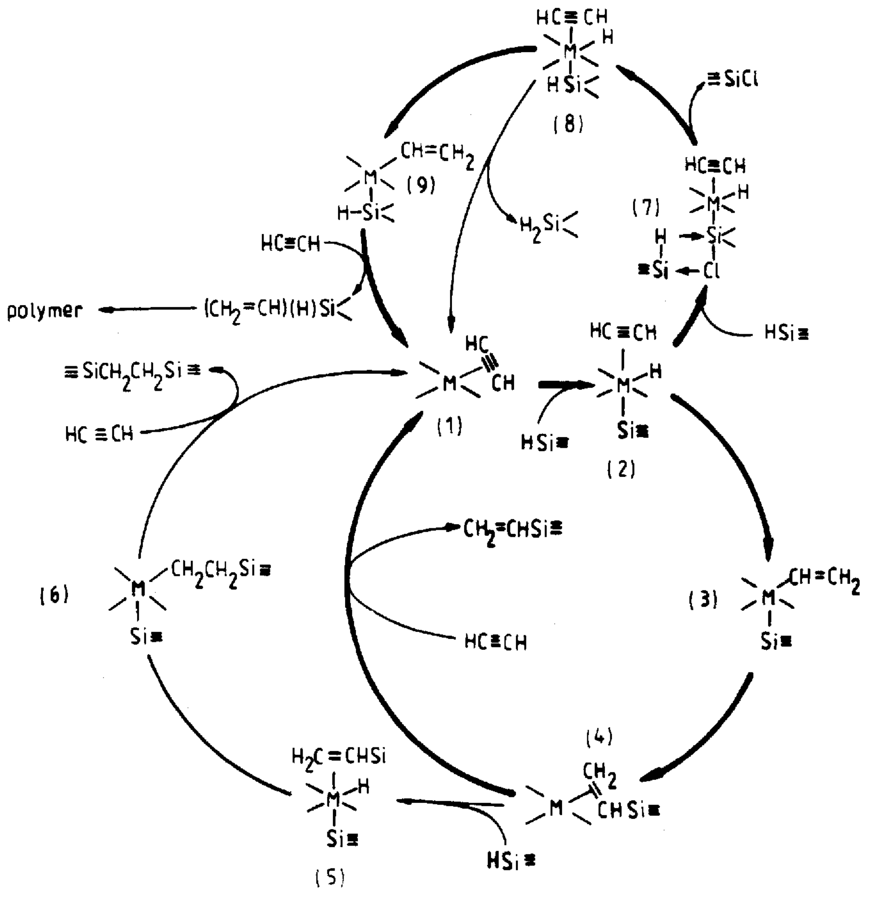
Figure 2 An example of GLC separation of reaction mixture. A. Acetylene hydrosilylation. B. Trichlorosilane redistribution.

Products of the addition of dichlorosilane to acetylene were not found by GLC presumably because of polyaddition of the $CH_2=CHSiHCl_2$ or further redistribution of H_2SiCl_2. Catalytic results, including the conversion of trichlorosilane (C_H) (the reaction was carried out in excess of acetylene), the yield of vinyltrichlorosilane (Y_1), as well as the selectivity (S_{1-4}) of the determined reaction products are summarized in Table 2.

Generally, rhodium complexes are more efficient than ruthenium ones. Under the hydrosilylation test used in this work the effect of variation of the functional group of the ligand linked to silica is small. For rhodium catalysts the most effective are the ligands involving diphenylphosphine (cat. A) and mercapto (B), but morpholine (D) and nitrile (C) also show good catalytic activity. Ruthenium complexes appear as less selective catalysts for the reactions examined, but again the ligand with diphenylphosphine (cat. E) and mercapto groups (G) gave the best activities.

All the data presented in Table 2 show that the hydrosilylation of acetylene is accompanied by some competitive–consecutive side reactions such as hydrosilylation of vinyltrichlorosilane and redistribution of the trichlorosilane. The latter is followed by hydrosilylation and/or hydrogenative hydrosilylation with dichlorosilane, finally yielding polymeric products and ethyltrichlorosilane, respectively.

The proposed scheme for this complex reaction (Scheme B) shows the initial metal complex with acetylene (1), which after oxidative addition of trichlorosilane gives the intermediate (2). The lower cycle shows further pathways proposed according to a commonly used general model for hydrosilylation,[19] giving, via intermediates (3) and (4), predominantly vinylsilane (and under local excess of trichlorosilane compared with



M = Rh, Ru

Scheme B

Table 2 Catalytic data for the reaction of trichlorosilane with acetylene

	115°C						140°C					
		S [%]						S [%]				
Catalyst	C_H [%]	1	2	3	4	Y [%]	C_H [%]	1	2	3	4	Y [%]
A	80	76	—	20	4	61	100	70	—	19	10	70
B	79	60	3	17	5	47	97	76	—	14	10	74
C	99	46	4	29	3	45	98	66	3	19	8	64
D	100	46	6	19	21	46	97	51	11	17	10	49
E	96	58	3	30	9	57	98	67	—	20	10	66
F	52	56	—	27	13	29	95	56	10	20	14	53
G	63	55	2	35	8	35	83	57	7	30	6	47
H	37	63	—	32	5	23	43	57	2	36	5	25

C_H—conversion of the hydrosilane.
S—selectivity.
Y—yield of the vinyltrichlorosilane determined by GLC flow rate: $f_{CH \equiv CH} = 22.8$ mmole h^{-1}, $f_{Si-H} = 2.8$ mmole h^{-1}, $m_{cat} = 0.6$ g.

vinylsilane also the double hydrosilylated product—bis(trichlorosilyl)ethane—via the intermediates (5) and (6)). The latter path is a well known process for hydrosilylation of vinyl-substituted silanes[2,3,9–11,19] in the presence of various metal complexes. Redistribution of trichlorosilane also occurs readily under such conditions, e.g. in the presence of nickel complex catalysts for hydrosilylation,[20] and therefore the proposed scheme (upper cycle) assumes formation of $SiCl_4$ via the intermediate (7). Instead of the dichlorosilanes which are absent in the reaction products, the scheme considers formation of vinyldichlorosilane which has not been isolated because of its fast intermolecular hydrosilylation. However, since the observed polymers were not yielded proportionally to $SiCl_4$ production, it seems probable that dichlorosilane can be also applied as a reducing agent for hydrogenation of acetylene or its hydrogenative hydrosilylation, resulting in the production of ethyltrichlorosilane. Separate experiments on the hydrosilylation of ethylene by trichlorosilane in the presence of the catalysts used indicated a very high yield of ethyltrichlorosilane. Thus, hydrogenation of acetylene to ethylene by dichlorosilane in the coordination sphere of the metal center appears to be the crucial stage of the reaction examined (which can also involve radical steps). Mechanistic studies on this subject are continuing.

Table 3 Effect of flow rate (f) of acetylene and trichlorosilane on the hydrosilane conversion (C_H), yield (Y), and selectivity (S) of the products (GLC) for the reaction catalyzed by the catalyst B

f [mmole h^{-1}]			S [%]				
HC≡CH	$HSiCl_3$	C_H [%]	1	2	3	4	Y [%]
24.0	3.2	93	74	1	15	10	67
20.5	2.0	83	81	—	19	—	67
19.8	2.4	79	94	—	6	—	74
19.8	2.4[a]	66	88	—	12	—	58
39.0	5.6	49	71	—	29	—	35
13.0	2.0	95	77	5	8	10	74
13.0	2.0[a]	70	80	—	19	—	56

[a] The catalyst 7-fold used (70 h on stream).
$t = 130$°C, $m_{cat} = 0.6$ g.

Occurrence of the side reactions depends predominantly on the reaction conditions, particularly the flow rate of substrates and their ratio. Thus, some of the side reactions can be eliminated by the reaction conditions (Table 3).

A relatively high flow of trichlorosilane at an average rate flow of the acetylene of 13–25 mmole h^{-1} favours the very high (close to 100%) conversion of trichlorosilane. A decrease in its flow rate causes the reaction to occur with practically no side hydrosilylation processes. Only a redistribution of the trichlorosilane is noted. On the other hand, an increase in the flow rate of both substrates declines markedly the conversion of trichlorosilane and, as a consequence, also of vinyltrichlorosilane. However, the $SiCl_4$ is one by-product observed.

After 70 h on stream the activity of the catalyst B decreased but all the side reactions except the redistribution were eliminated.

It can be concluded that the smooth variation of the conditions of the reactions (particularly flow rates as well as temperature) can supply very active and selective catalysts for synthesis of vinyltrichlorosilane in the gas-phase. Kinetic measurements of the reaction enabled us to determine the initial rates of hydrosilylation of acetylene by trichlorosilane (r), which are actually the parameters of the catalytic activity of the heterogenized rhodium and ruthenium complexes in the reaction leading to the synthesis of vinyltrichlorosilane (Table 4).

Table 4 Catalytic activity (r) of the catalysts A, B and F and activation energy in the hydrosilylation reaction of acetylene by trichlorosilane

	r [cm^3 g^{-1} s^{-1}]		
Catalyst	115°C	140°C	E_a [kJ mol^{-1}]
A	1.05	1.55	22.6 ± 3.8
B	1.28	1.87	20.5 ± 2.1
F	0.87	1.44	27.6 ± 3.3

$\Delta r = 0.03$.

Determination of r in the temperature range 100–160°C allows us to plot the Arrhenius dependence r vs. 1/T (Fig. 3) to evaluate from these plots the apparent activation energy E_a. The data obtained for selected catalysts (Table 4) show the small enhancement of the rate with the temperature and they are comparable with the respective data obtained earlier by Kraus from a study of the reaction catalyzed by chloroplatinic acid supported on a styrenedivinylbenzene copolymer substituted with a cyanomethyl group ($E_a = 18.4$ kJ mole^{-1}).[4,5]

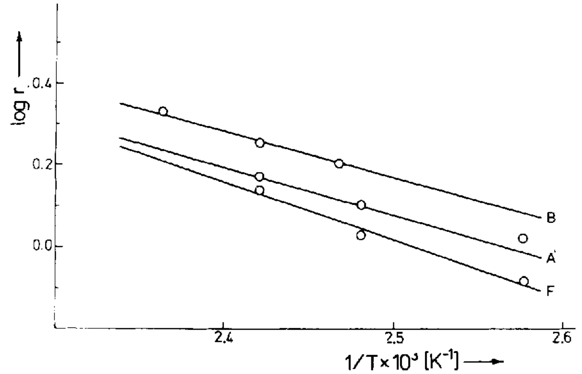


Figure 3 Arrhenius plot for gas-phase hydrosilylation of acetylene by trichlorosilane.

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