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Catalysis of hydrosilylation

XX *. Unusual reaction of vinyltriethoxysilane with triethoxysilane catalyzed by nickel acetylacetonate

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Abstract

Nickel acetylacetonate is shown to be a catalyst of an unusual reaction of vinyltriethoxysilane with triethoxysilane involving formation of bis(silyl)ethene and bis(silyl)butanes as the main products accompanied by others of direct and dehydrogenative hydrosilylation, bis(silyl)ethane and ethylsilane as well as products of redistribution of triethoxysilane and formation of oligomers. The latter reaction is a consequence of consecutive oligomerization of bis(silyl)ethenes and other products. The effect of temperature, the concentration ratio of substrates and the catalyst, and other reaction conditions on the conversion and reaction yield led us to propose a scheme explaining the course of this competitive-consecutive reaction.

Introduction

Nickel salts and complexes are well known catalysts of hydrosilylation, although less active and selective than the commonly used platinum complexes, e.g. the Speier catalyst [1]. A characteristic feature of the catalysis of hydrosilylation by nickel compounds is the formation of a mixture of α and β -adducts [1,2]. The reaction of hydrosilylation of vinylsubstituted silanes catalyzed by platinum complexes predominantly gives β -adducts, and is accompanied by an exchange of substituents on silicon at both substrates [3,4]. The latter side reaction also occurs in the presence of other transition metal complexes [5,6].

Our preliminary studies on the reaction of vinyltriethoxysilane with triethoxysilane in the presence of $\text{Ni}(\text{acac})_2$ have shown that the simple hydrosilylation product is accompanied by others (unsaturated and oligomeric) that can be of great importance in the synthesis of organosilicon compounds [5].

Extensive studies on Ni-complexes containing ligands as acac [7], olefins and dienes [8] show high activities for dimerization (or oligomerization) of olefins, but usually in the presence of Lewis acids such as alkylaluminium halides [9,10].

* Part XIX see ref. 17.

The works published by Yur'ev et al. on dimerization (oligomerization) of vinylsilanes revealed a high activity of the $\text{Ni}(\text{acac})_2\text{-AlEt}_n\text{Cl}_{3-n}\text{-PPh}_3$ system (contrary to $\text{Ni}(\text{acac})_2$ alone) in the dimerization of vinyltrimethylsilane [11,12] and a high activity of the system $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-AlEt}_3\text{-PPh}_3$ in dimerization of vinyltrimethoxy- and vinyltrichlorosilanes [11] as well. The systems based on Ni salts are not effective in the latter reactions. All mentioned dimerizations give isomers of bis(silyl)butenes in yields even above 80%.

Regarding the above results this work evaluates the main pathways of the new competitive-consecutive reaction of vinyltriethoxysilane with triethoxysilane in the presence of nickel acetylacetonate catalyst.

Experimental

Materials

Triethoxysilane and tetraethoxysilane were obtained by alcoholysis of SiHCl_3 and SiCl_4 , respectively, according to a standard procedure. Vinyltriethoxysilane and ethyltriethoxysilane (Fluka) and $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Ni}(\text{acac})_2$ and other catalysts (Pierce) were obtained commercially and used without further purification. Bis(triethylsilyl)ethene was obtained by metathesis of vinyltriethoxysilane in the presence of $\text{RuCl}_2(\text{PPh}_3)_2$ catalyst [13] and bis(triethoxysilyl)ethane by hydrosilylation of the respective vinylsilane catalyzed by a Pt complex [5].

Equipment and analytical measurements

^1H and ^{13}C NMR spectra were recorded on a FX 909 Jeol spectrometer equipped with a Texas 9880 B computer system. Chromatography was performed on GCHF apparatus with 2 m steel column filled with 10% SE-30 on Chromosorb P.

Synthetic and catalytic procedures

General procedure. The catalyst ($\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Ni}(\text{acac})_2$ anh.) was placed in a glass ampoule (or in a flask equipped with a condensor) and a mixture of vinyltriethoxysilane and triethoxysilane was then added. Sealed ampoules (or flasks) were heated at given temperatures (more than 100°C) or under reflux (flasks) for several hours. Conversions of substrates and yields of the reaction products were calculated on the basis of the GLC analysis of the reaction mixture. All products were distilled under vacuum.

Results

The reaction of vinyltriethoxysilane with triethoxysilane proceeds in both closed and open systems in the presence of nickel acetylacetonate catalyst predominantly at temperatures over 100°C . Chromatographic analysis of the post-reaction mixture indicates the presence of some products at almost quantitative conversion of substrates, at the optimum concentration of the latter and of the catalyst, and at given temperatures. A typical chromatogram of such a mixture is shown in Fig. 1.

Most of the products were identified by comparing the retention times of their peaks with those of standards. The main reaction products are the following: bis(triethoxysilyl)ethene (IV), bis(triethoxysilyl)methylpropane (VI) and bis(triethoxysilyl)butane (VII) (the last two were for the first time isolated via preparative

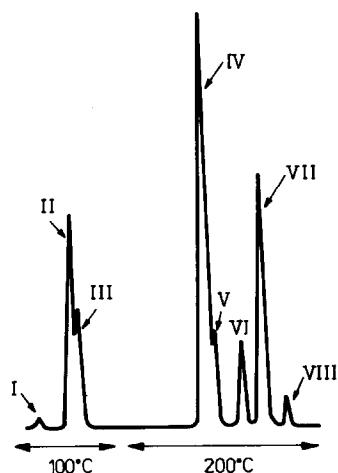


Fig. 1. An example of GC separation of the reaction mixture occurring in reflux: (0) $\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$; (I) $\text{HSi}(\text{OC}_2\text{H}_5)_3$; (II) $\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$; (III) $\text{Si}(\text{OC}_2\text{H}_5)_4$; (IV) $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}=\text{CHSi}(\text{OC}_2\text{H}_5)_3$; (V) $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$; (VI) $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$; (VII) $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_4\text{Si}(\text{OC}_2\text{H}_5)_3$; (VIII) high boiling products.

chromatography—see Table 1) as well as ethyltriethoxysilane (II) and bis(triethoxysilyl)ethane (V).

We also observed redistribution products of triethoxysilane—tetraethoxysilane (III) and product(s) boiling at higher temperatures (VIII). As a matter of fact no α -product of the hydrosilylation of vinylsilane, i.e. bis(triethoxysilyl)methylmethane was observed. A typical course of the reaction in the open and closed systems under various conditions, is illustrated by the results shown in Table 2.

Table 1

Spectroscopic data of isolated bis(silyl)butanes (CDCl_3 as a solvent)

Formula	^1H (δ , ppm) (TMS)	^{13}C (δ , ppm)
$ \begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ (\text{CH}_3\text{CH}_2\text{O})_3\text{SiCHCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3 \\ \\ \text{CH}_3 \\ 8 \end{array} $		
CH_3- (C_1, C_7)	1.24 (t, 18H)	18.23 (q)
$-\text{CH}_2\text{O}-$ (C_2)	3.82 (q, 12H)	58.62 (t)
$-\text{CH}_2\text{O}-$ (C_6)		58.46 (t)
$-\text{CH}_2-$ (C_4)		13.65 (t)
	1.07–0.64 (m, 4H)	
$-\text{CH}_2\text{Si}$ (C_5)		9.58 (t)
$-\text{CHSi}-$ (C_3)	1.97–1.29 (m, 2H)	21.37 (d)
CH_3- (C_8)	1.22–1.08 (d, 3H)	20.04 (q)
$(\text{CH}_3\text{CH}_2\text{O})_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$		
$-\text{CH}_3$	1.22 (t, 18H)	18.26 (q)
$-\text{CH}_2\text{O}-$	3.81 (q, 12H)	58.35 (t)
$-\text{CH}_2-$	1.30–1.62 (m, 4H)	26.44 (t)
$-\text{CH}_2\text{Si}-$	1.11–0.42 (m, 4H)	10.40 (t)

Table 2

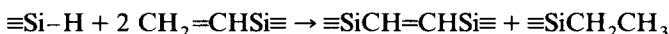
The effect of reaction conditions on the conversion of substrates and yield of products

Substrates and products	Reflux		120 °C		120 °C ampoules	
	0.25 h	1 h	0.25 h	1 h	0.25 h	1 h
<i>Conversion (%)</i>						
HSi≡	100	100	77	86	62	63
ViSi≡	100	100	100	100	100	100
<i>Yield (%)</i>						
CH ₃ CH ₂ Si≡	11	13	10	11	11	13
(C ₂ H ₅ O) ₄ Si	14	15	8	8	6	5
<i>trans</i> ≡SiCH=CHSi≡	32	24	25	17	19	18
≡SiCH ₂ CH ₂ Si≡	7	7	11	14	10	15
≡SiCH(CH ₃)CH ₂ CH ₂ Si≡	7	7	7	7	6	6
≡Si(CH ₂) ₄ Si≡	21	22	20	20	16	17
high boiling products	8	12	4	6	1	5

[HSi≡]:[CH₂=CHSi≡]:[Ni(acac)₂] = 1:1:3·10⁻³. -Si≡ denotes -Si(OC₂H₅)₃.

It is interesting that the ratio bis(silyl)ethene/bis(silyl)ethane depends on the temperature used. When the reaction occurs under reflux (temp. 70–200 °C) much more bis(silyl)ethene (IV) is formed, while at 120 °C, especially under closed system, amounts of β are comparable with IV. Yields of bis(silyl)butanes (VI + VII) do not markedly depend on the temperature and systems used.

Bis(silyl)ethene (IV) is probably mainly formed as a result of dehydrogenative silylation, since it is accompanied by ethyltriethoxysilane. However, the amount of the latter is smaller in comparison with the amount shown by the stoichiometric equation presented below.



Concentration of IV has been decreased during the reaction, while the concentration of highly boiling products (oligomers) has been increased. This might be caused by polymerization of IV, especially at higher temperatures, and/or by redistribution of triethoxysilane which gives, besides (C₂H₅O)₄Si oligomeric products of (C₂H₅O)₂SiH₂ of high reactivity. The best depiction of the change in concentration of products and substrates against time is given in Fig. 2. The reaction occurring under reflux is shown.

It is very interesting that, contrary to the studies of Yur'ev et al. [11] on the reaction catalyzed with organometallic compounds of the Ziegler type, we did not observe any products of direct dimérisation of vinylsilanes leading to the synthesis of bis(silyl)butenes (not even as intermediates).

Yet, the ratio and amounts of particular products strongly depend on those of both substrates, hydrosilane and vinylsilane.

The results presented in Table 3 show directions of changes suggesting that several competing reactions occur simultaneously.

Nickel acetylacetonate used as catalyst in these competing reactions shows extremely high activity at higher temperatures. Treatment of nickel(II) salts with silicon hydride generally leads to intermediates with hydrogen–nickel–silyl bonds, which, owing to their kinetic lability, lead to nickel(0) complexes by reductive

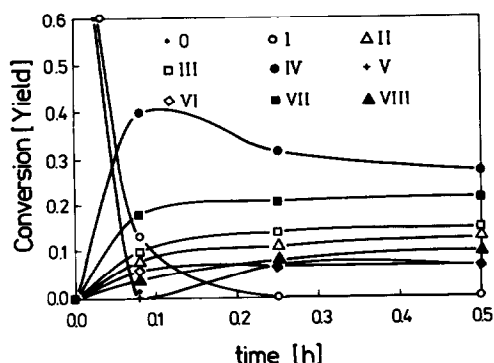


Fig. 2. Change in conversions of substrates and yields of products against time of the reaction examined (for notations of substrates and products see Fig. 1).

elimination [1,5]. During the reaction it is observed that the nickel precipitates from the reaction mixture, but most products are formed within a few minutes in the reaction occurring at a temperature above 100°C , so the real catalyst is assumed to be a labile Ni^0 complex with vinylsilane as a ligand.

Discussion

This new pathway of the hydrosilylation of vinylalkoxysilanes leading to the synthesis of a large amount of bis(silyl)ethenes and bis(silyl)butanes in the presence of nickel salt may be explained by two parallel reactions of dehydrogenative silylation and hydrogenative dimerization of vinylsilanes at the metal center, as shown in Scheme 1.

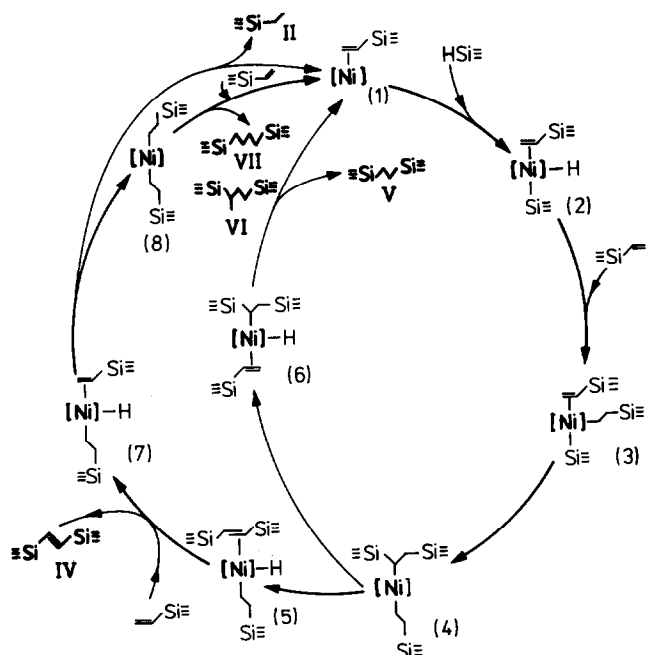
This mechanism postulates the existence of a complex of nickel with vinylsilane (1), to which in the catalytic cycle (following preliminary reduction of Ni^{II} to Ni^0), hydrosilane (2) is added oxidatively. This is followed by the coordination of the

Table 3

Effect of $\equiv\text{SiH}/\equiv\text{SiCH}=\text{CH}_2$ ratio on the conversion of substrates and the yield of products

Substrates and products	Ratio $\text{HSi}\equiv : \text{ViSi}\equiv$				
	0.1:1	0.3:1	0.5:1	1:1	2:1
<i>Conversion (%)</i>					
$\text{HSi}\equiv$	100	100	87	64	45
$\text{ViSi}\equiv$	44	85	100	100	100
<i>Yield (%)</i>					
$\text{CH}_3\text{CH}_2\text{Si}\equiv$	—	13	14	14	15
$(\text{C}_2\text{H}_5\text{O})_4\text{Si}\equiv$	4	4	5	5	6
<i>trans</i> $\equiv\text{SiCH}=\text{CHSi}\equiv$	10	29	35	19	16
$\equiv\text{SiCH}_2\text{CH}_2\text{Si}\equiv$	—	—	6	9	10
$\equiv\text{SiCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Si}\equiv$	2	6	8	6	6
$\equiv\text{Si}(\text{CH}_3)_4\text{Si}\equiv$	10	22	23	17	19
high boiling products	1	3	3	7	7

$[\text{CH}_2=\text{CHSi}\equiv]:[\text{Ni}(\text{acac})_2] = 1:3 \cdot 10^{-3}$; ampoules, 120°C , 2 h. $-\text{Si}\equiv$ denotes $-\text{Si}(\text{OC}_2\text{H}_5)_3$.



Scheme 1. Proposed mechanism of the competitive-consecutive reaction of vinyltriethoxysilane with triethoxysilane catalyzed by nickel acetylacetonate.

second molecule of vinylsilane (3). In comparison with an analogous reaction catalyzed by ruthenium compounds [15] a complex with a σ -ethylsilyl ligand is observed. (σ -complex (3)) which does not undergo reductive elimination owing to strong coordination of vinylsilane. Transfer of the silyl group from the metal to the latter molecule results in the formation of complex 4. Furthermore, the reaction may proceed via two different pathways. At the nickel center, hydrogen transfer from the α -silyl- β -ethylsilyl ligand to the metal is more likely to occur [14], leading to the formation of unsaturated products of bis(silyl)ethene coordinated to nickel (5). The second pathway (less probable regarding the result) involves hydrogen transfer from β -ethylsilyl, leading, via the formation of hydrogen compounds (6), to bis(silyl)ethane as the product. The exchange of bis(silyl)ethene ligands with vinylsilane results in the formation of complex 7. This complex may eliminate ethylsilane (II) and regenerate the initial catalyst, as in the reaction at the ruthenium center [15]. However, the formation of the complex by insertion of vinylsilane into the Ni-H bond (8) precedes the elimination of bis(silyl)butanes (VI + VII).

To make Scheme 1 more clear it does not contain the nickel complexes with the isomeric α -methylsilyl ligand $[\text{Ni}]-\text{CH}(\text{CH}_3)\text{Si}\equiv$ that can be formed (due to the Ni-complex catalyzed reaction [1,2]) via one of the pathways $2 \rightarrow 3$ and $7 \rightarrow 8$ competitively with those shown in Scheme 1, yielding isomeric bis(silyl)butane—VII instead of VI. The above diagram explains the yields of silyl derivatives of butanes without butenes formation.

Formation of bis(silyl)ethenes may also occur in the metathesis of vinylsilane as in the case of ruthenium catalysts [16] according to the following equation:



And, although no ethylene was observed during the reaction it cannot be excluded that the ethylene yielded can be an initiator of the direct formation of the ethylsilylnickel complex **8** with the elimination of silylbutanes parallelly to the reaction cycle involving dehydrogenative silylation.

Further detailed studies should aim at quantitative evaluation of the contribution of each of the pathways in the proposed mechanism of the reaction studied.

Acknowledgements

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