# Hydrosilylation of Allyl Ethers in the Presence of Platinum(II) Immobilized on Polymethylene Sulfide

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**Abstract**—The reactions of allyl ethyl, allyl butyl, allyl glycidyl, allyl benzyl, and allyl phenyl ethers with 1,1,3,3-tetramethyldisiloxane in the presence of platinum(II) immobilized on polymethylene sulfide have been studied.

Keywords: hydrosilylation, allyl ethers, tetramethyldisiloxane, immobilized platinum(II) complex, polymethylene sulfide

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Catalytic hydrosilylation of olefins is a key reaction in the production of industrially important organosilicon compounds generated in the presence of platinum complexes. Since the price of platinum is high and unstable, its repeated use is desirable, which is possible with prolonged operation of the metal complexes. The use of immobilized systems is among the approaches to the stabilization of the catalytic properties and the multiple use of the catalysts.

A large variety of the supported platinum and rhodium complexes have been developed, due to their wide use and efficiency in olefins hydrosilylation [1–3]. Some of the suggested methods are multistage and laborious, which significantly increases their price and levels off the advantages.

Herein we studied the platinum(II) complex on a polymer carrier (polymethylene sulfide [Pt–PMS]) (Scheme 1) as an alternative supported catalyst. Polymethylene sulfide which is formed during oil purification of hydrogen sulfide is an efficient complexing agent with sulfur atoms uniformly distributed along the polymer chain and can act as a macroligand (sulfide or alkylthiolate type). The chemisorption of  $K_2PtCl_4$  on polymethylene sulfide is accompanied by the formation of the immobilized *cis*-complex. Polymethylene sulfide has been successfully used in certain regions of Russia as a sorbent of heavy metals from used catalysts (gold, platinum, and palladium), tailings and wash waters of catalyst factories (palladium and silver) as well as in the processing of

photomaterials [4], and the [Pt–PMS] complex revealed good properties in vinylsiloxanes hydrosilylation [5].

In view of the rapid growth of the fields of organosilicon compounds applications and, hence, the broadening of the demanded substrates range, it was reasonable to investigate the catalytic activity of [Pt–PMS] towards hydrosilylation of allyl glycidyl (AllOGlyc), allyl phenyl (AllOPh), allyl benzyl (AllOBn), allyl ethyl (AllOEt), and allyl butyl (AllOBu) ethers with 1,1,3,3-tetramethyldisilocane. The AllOGlyc ether was of special importance since epoxysilanes and epoxysiloxanes formed upon its hydrosilylation was used as materials for electronics, ship coatings, semipermeable membranes, materials with reduced flammability, aerospace materials, etc. [6, 7].

Hydrosilylation of allyl ethers with 1,1,3,3-tetramethyldisiloxane in the presence of [Pt–PMS] occurs predominantly with the formation of the  $\gamma$ - and  $\gamma$ , $\gamma$ -addition









 $m, n = 1-4; m \ge n; R = Et, Bu, Glyc ( \bigcirc CH_2), Bn, Ph.$ 

products, i. e. via anti-Markovnikov addition of a single or both SiH groups of the hydrosiloxane (Scheme 2). The  $\beta$ -,  $\beta$ , $\beta$ -, and  $\beta$ , $\gamma$ -addition products are formed in much lesser amount, which is typical of hydrosilylation in the presence of platinum catalysts [8].

On top of the major reaction, allyl ethers are prone to the allyl-propenyl isomerization and reduction, and 1,1,3,3-tetramethyldisiloxane is disproportionated into linear siloxanes HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (n = 2–4); moreover, allyl ethers hydrosilylation with the formed siloxanes HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H occurs similar to hydrosilylation with the starting (HMe<sub>2</sub>Si)<sub>2</sub>O. Such side transformation of the allyl ethers and (HMe<sub>2</sub>Si)<sub>2</sub>O is in line with the general features of hydrosilylation with homogeneous or heterogeneous platinum and rhodium complexes, whereas other side reactions (epoxide cycle opening and formation of glycidyl acrylate [9, 10],  $\alpha$ -addition [8], dehydrogenative silylation [11, 12], propene elimination [10], dimerization and polymerization of ethers [8, 11, 13, 14], siloxanes cyclization [15], etc.) did not occur in the presence of the catalytic systems obtained by us.

Kinetic curves of the interaction of the allyl ethers with  $(HMe_2Si)_2O$  were S-shaped, revealing the induction period and the hydrosilylation stages differing in the rate (Fig. 1). The induction period was likely related to the poor availability of platinum in the complex with polymethylene sulfide; the subsequent low-rate stage was due to slow formation of the true catalyst, and the high-rate stage corresponded to accumulation of sufficient amount of the catalytically active species.

The induction period duration was related to the nature of substituent R in the allyl ether AllOR, the catalyst concentration, and temperature. The shortest induction period was observed during hydrosilylation of AllOGlyc at 120°C (35 min,  $c_{\text{Pt}} = 3 \times 10^{-3} \text{ mol/L}$ ) (Figs. 1 and 2, Table 1). Decrease in the temperature by 20°C increased the induction period by 10 min (45 min, 100°C), and the decrease in the temperature to 80°C added further 10 min

	Time, h	<i>T</i> , ℃	Conversion of AllOR, %	$\gamma_{\Sigma}$ -Selectivity, %	γ/β, %	Catalyzate composition, %							
Ether						product of (HMe <sub>2</sub> Si) <sub>2</sub> O addition					CH <sub>3</sub> CH=CHOR	others	
						β-	γ-	β,β-	β,γ-	γ,γ-			
AllOBu	8.00	120	99	96.1	97.3/2.7	1.5	60.2	0.4	0.4	13.4	0.2	23.9	
AllOEt	7.75	120	98	95.3	99.7/0.3	0.2	59.2	0.0	0.0	14.2	4.0	24.4	
AllOBn	8.00	120	90	89.8	97.0/3.0	1.7	56.7	0.0	0.5	14.3	4.6	22.2	
AllOPh	22.00	120	97	89.8	92.1/7.9	3.9	45.2	0.3	1.3	16.1	3.1	30.1	
AllOGlyc	1.25	120	94	86.4	99.0/1.0	0.6	60.3	0.0	0.0	17.3	6.0	15.8	
	1.67 <sup>b</sup>	120	98	93.8	95.2/4.8	3.2	63.6	0.0	0.0	16.2	4.3	12.7	
	2.30	100	91	95.4	88.4/11.6	3.2	65.0	0.0	0.0	9.5	6.2	16.1	
	6.50 <sup>b</sup>	100	91	89.3	92.5/7.5	5.4	61.6	0.0	2.0	13.8	5.2	12	
	7.00	80	92	92.1	81.9/18.1	5.2	61.0	0.0	0.0	9.0	5.2	19.6	

Table 1. Hydrosilylation of allyl ethers with 1,1,3,3-tetramethyldisiloxane in the presence of [Pt–PMS]<sup>a</sup>

<sup>a</sup>  $c_{\text{Pt}} = 3 \times 10^{-3} \text{ mol/L}$ , ether : siloxane molar ratio = 1 : 1.5. <sup>b</sup>  $c_{\text{Pt}} = 3 \times 10^{-4} \text{ mol/L}$ .

to the induction period (55 min) (Fig. 2). Decrease in the catalyst concentration by an order of magnitude increase the induction period by 5 min at 120°C, and fivefold at 100°C (to 3 h). Hence, the optimal temperature for the [Pt–PMS]-assisted hydrosilylation with 1,1,3,3-tetra-methyldisiloxane was 100–120°C ( $c_{Pt} = 3 \times 10^{-3} \text{ mol/L}$ ). AllOGlyc hydrosilylation with polysiloxane containing silicon hydride groups in the presence of H<sub>2</sub>PtCl<sub>6</sub> (the Speier catalyst) occurs at close temperature (110–130°C) [16], whereas temperature optimal for hydrosilylation of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (HMe<sub>2</sub>Si)<sub>2</sub>O on [Pt–PMS] was significantly lower (55°C; the decrease in temperature to 45°C has led to the appearance of the induction period) [5].

The induction period during hydrosilylation of AllOEt and AllOBu was significantly longer than for AllOGlyc: 5 and 6.75 h, respectively (120°C,  $c_{Pt} = 3 \times 10^{-3} \text{ mol/L}$ ). The induction period duration was strongly affected by the distance between the phenyl ring and the allyl group: the induction period during hydrosilylation of AllOPh was the longest (20 h, 120°C,  $c_{Pt} = 3 \times 10^{-3} \text{ mol/L}$ ), whereas that during the interaction between AllOBn and 1,1,3,3-tetramethyldisiloxane was close to the induction period for AllOEt (5.5 h, 120°C,  $c_{Pt} = 3 \times 10^{-3} \text{ mol/L}$ ). Hence, the induction period during the hydrosilylation was shortened over the following ethers series: AllOPh >> AllOBu >> AllOBn > AllOEt >> AllOGlyc. The highest conversion of AllOGlyc was reached within 1.25 h (94%, 120°C,  $c_{Pt} = 3 \times 10^{-3}$  mol/L), and duration of its hydrosilylation (excluding the induction period) was the shortest among the probed ethers (35– 40 min). The decrease in the reaction temperature to 100°C increased the hydrosilylation duration by 2.4– 2.7 times (95 min, conversion 91%, Fig. 2), further decrease in the temperature being even more critical (6 h, conversion 92%, 80°C). The decrease in the [Pt–PMS] concentration had weaker effect on the reaction rate in comparison with temperature. The decrease in  $c_{Pt}$  by an order of magnitude increased the hydrosilylation duration by 1.5–1.7 times at 120°C (60 min, conversion 98%), yet the reaction duration was significantly increased at 100°C (3.5 h, conversion 91%).

The maximum conversion of AllOBu (99%, 8 h, 120°C) was higher than that of AllOGlyc, and the hydrosilylation occurred within 1.25 h (excluding the induction period) (Table 1). Hydrosilylation of AllOEt was slower (~2 h), and the conversion upon the reaction completion (7 h) reached 94% (Figs. 1 and 3). Kinetic curve of the AllOBn hydrosilylation was practically identical to that of AllOEt (reaction duration of 2 h). The slope of the hydrosilylation kinetic curve and, hence, the reactivity of allyl phenyl ether was the lowest among the studied ethers. Hence, the allyl ethers reactivity in the hydrosilylation



**Fig. 1.** Kinetics of the change in ethers conversion during their interaction with  $(HMe_2Si)_2O$  in the presence of [Pt-PMS] ( $c_{Pt}=3\times10^{-3}$  mol/L, ether : siloxane molar ratio = 1 : 1.5, 120°C). (1) AllOGlyc, (2) AllOEt, (3) AllOBn, (4) AllOBu, and (5) AllOPh.

was decreased along the following series: AllOGlyc > AllOBu > AllOEt  $\approx$  AllOBn > AllOPh.

Allyl-propenyl isomerization and reduction of allyl ethers accompanying the hydrosilylation was determined by the nature of the R substituent in the AllOR ether. The highest yield of the geometry isomers of the propenyl ethers was observed for AllOGlyc. When the hydrosilylation was complete, the fraction of the propenyl glycidyl ethers was as high as 6.0%; the decrease in neither the reaction temperature nor [Pt–PMS] concentration led to significant decrease in the side products amount. The fraction of the reduction product (propyl glycidyl ether) was also relatively high (3.6%) and was independent of the reaction temperature and catalyst concentration. The side reactions of AllOGlyc were in line with its high reactivity.

Hydrosilylation of AllOBu led to the formation of only trace amounts of the isomerization and reduction products (120°C); their fraction did not exceed 0.2% upon the reaction completion. The yield of propenyl butyl ethers upon the induction period reached 0.9%. The decrease in the propenyl ethers yield during the hydrosilylation is typical of other allyl ethers as well and is due to their consumption for the hydrosilylation into the  $\beta$ -adduct [17]. Hence, the reaction selectivity is reduced. However, the low concentration of the propenyl ethers in the presence of [Pt–PMS] and the lower activity of the *endo*-C=C bonds in the hydrosilylation in comparison with the terminal ones [14, 18–20] led to suggestion of insignificant contribution of the propenyl ethers hydrosilylation.



**Fig. 2.** Kinetics of the change in allyl glycidyl ether conversion during its interaction with  $(HMe_2Si)_2O$  in the presence of [Pt–PMS] (ether : siloxane molar ratio = 1 : 1.5) at  $c_{Pt} = 3 \times 10^{-3}$  (1, 3, 4),  $3 \times 10^{-4}$  mol/L (2, 5). (1, 2) 120°C, (3, 5) 100°C, and (4) 80°C.

Isomerization of AllOEt was much more prominent than for AllOBu. The fraction of the propenyl ethyl ethers upon the reaction completeness was higher than that of propenyl butyl ethers by 20 times (4.0%), propyl ethyl ether was not formed. In its turn, isomerization and reduction of AllOBn was twofold faster than those of AllOEt (8.0% in total, 8 h, 120°C), which reduced the selectivity of AllOBn hydrosilylation in comparison with AllOEt and AllOBu.

Side transformations of AllOPh were limited to the formation of propenyl phenyl ethers (3.1%); probably, they were formed in larger amount but were consumed



**Fig. 3.** Kinetics of the change in ethers conversion after the induction period during their interaction with  $(HMe_2Si)_2O$  in the presence of [Pt–PMS] ( $c_{Pt}=3\times10^{-3}$  mol/L, ether : siloxane molar ratio = 1 : 1.5, 120°C). (1) AllOGlyc, (2) AllOBu, (3) AllOEt, (4) AllOBn, and (5) AllOPh.

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<i>T</i> , °C	Ether	Time h	<i>n</i> =	= 2	<i>n</i> =	= 3	<i>n</i> = 4	
1, 0		1 1110, 11	A	В	А	В	А	В
80	AllOGlyc	1.00	1.9	1.9	0.3	0.3	0.0	0.0
80	AllOGlyc	7.00	0.3	2.2	2.0	3.8	0.3	0.4
100	AllOGlyc	0.75	1.2	1.2	0.2	0.2	0.0	0.0
100	AllOGlyc	2.30	0.3	2.2	1.9	3.6	0.2	0.4
100	AllOGlyc	3.00 <sup>b</sup>	4.5	4.5	1.7	1.7	0.6	0.6
100	AllOGlyc	6.50 <sup>b</sup>	0.3	2.3	1.2	2.9	0.2	0.5
120	AllOGlyc	0.50	4.7	4.7	1.2	1.2	0.0	0.0
120	AllOGlyc	1.15	0.3	3.3	0.9	3.1	0.1	0.1
120	AllOGlyc	0.67 <sup>b</sup>	1.9	1.9	0.5	0.5	0.0	0.0
120	AllOGlyc	1.67 <sup>b</sup>	0.0	3.1	0.6	1.4	0.7	0.8
120	AllOBu	5.00	10.7	10.7	3.7	3.7	1.1	1.1
120	AllOBu	6.75	9.3	11.8	6.3	6.3	1.8	2.1
120	AllOBu	7.00	3.3	13.1	1.7	3.5	0.6	0.9
120	AllOEt	5.00	14.4	15.6	2.9	3.3	0.3	0.3
120	AllOEt	7.75	1.2	14.8	1.5	3.1	0.4	0.4
120	AllOBn	5.50	6.7	7.1	5.3	5.3	0.7	0.7
120	AllOBn	9.00	0.6	11.7	0.8	2.1	0.2	1.1
120	AllOPh	20.00	42.6	43.8	1.9	1.9	0.6	0.6
120	AllOPh	22.00	18.8	27.7	0.6	5.9	0.4	2.2

**Table 2.** Yield of  $HMe_2Si(OSiMe_2)_nH$  (n = 2-4) in hydrosilylation of allyl ethers with 1,1,3,3-tetramethyldisiloxane in the presence of [Pt–PMS]<sup>a</sup>

<sup>a</sup>  $c_{\text{Pt}} = 3 \times 10^{-3} \text{ mol/L}$ , ether : siloxane molar ratio = 1 : 1.5. A—yield of free siloxane HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H, B—total yield of free siloxane HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H and siloxane bound into hydrosilylation products. <sup>b</sup>  $c_{\text{Pt}} = 3 \times 10^{-4} \text{ mol/L}$ .

for hydrosilylation into the  $\beta$ -adduct, coinciding with low regioselectivity of AllOPh hydrosilylation.

Another side reaction accompanying the hydrosilylation is the disproportionation of the starting hydrosiloxane into HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (n=2–4) which are prone to hydrosilylation of the allyl ether, the products fraction being up to 30%. The major part of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H is formed during the induction period, depending on the induction period duration, temperature, and the metal complex concentration, and is indirectly related to the reactivity of the ether affecting the target reaction duration.

Side transformations of 1,1,3,3-tetramethyldisiloxane during AllOGlyc hydrosilylation were the least prominent, due to the shortest induction period and the overall duration of the target reaction. The total yield of the formed HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H, in view of their consumption for the interaction with AllOGlyc, upon the hydrosilylation completeness was 3.3, 3.1, and 0.1% (n=2, 3, and 4 respectively, 1.15 h at 120°C, Table 2). The decrease in temperature by 20°C reduced the trisiloxane yield to 2.2%, but the total yield of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>4</sub>H was increased. As a result, the total amount of the products of side transformation of the starting siloxane was only slightly decreased (by 0.5%). Further decrease in temperature by 20°C (to 80°C) practically did not affect the total yield of the products

of  $(HMe_2Si)_2O$  side transformations. The decrease in [Pt–PMS] concentration by an order of magnitude reduced the total yield of  $HMe_2Si(OSiMe_2)_3H$  by 1.5 times at 100°C (Table 2).

The addition of (HMe<sub>2</sub>Si)<sub>2</sub>O to AllOBu showed long induction period and the hydrosilylation duration, and the disproportionation was more prominent than in the case of AllOGlyc, allowing to monitor the dynamics of formation and consumption of the side siloxanes. The yield of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H, HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H, and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>4</sub>H was 10.7, 3.7, and 1.1%, (after 5 h at 120°C) and 9.3, 6.3, and 1.8% (after 6.75 h), respectively, i. e. HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H was consumed and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H was accumulated. When AllOBu was completely consumed, the yield of the side siloxanes was 3.3, 1.7, and 0.6%, due to their consumption in the hydrosilylation. Those processes are better illustrated by the kinetic curves (Fig. 4). For example, the kinetic curve of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H accumulation showed initial smooth growth, followed by steep decrease at certain concentration of the metal complex sites (the end of the induction period) at the high-rate hydrosilylation stage and then by smooth increase again. Only trace amount of the AllOBu hydrosilylation with 1,1,3,3,5,5-hexamethyltrisiloxane was formed during the induction period as reflected in the corresponding kinetic curve, followed by steep accumulation of the product (high-rate hydrosilylation) and leveling off (completeness of the hydrosilylation). Kinetic curve of the change in the total amount of free and hydrosilylated 1,1,3,3,5,5-hexamethyltrisiloxane [it was impossible to determine the consumption of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H for disproportionation] revealed smooth growth over the whole reaction duration. The curves of accumulation and consumption of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (n = 3, 4) were similar; total yield of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (accounting for the hydrosilylation) was 13.1, 3.5, and 0.9% (n = 2, 3, and 4, respectively; Table 2).

The accumulation of free  $HMe_2Si(OSiMe_2)_nH$  during the induction period and their consumption for the hydrosilylation was typical also of AllOEt and AllOBn reactions, the total yield of the siloxanes upon the reaction being practically equal to that for AllOBu (Table 2).

The longest induction period for the hydrosilylation of AllOPh led to the most prominent side transformation of hydrosiloxanes as compared to other ethers. When the induction period was complete, the yield of  $HMe_2Si(OSiMe_2)_nH$  was 42.6, 3.5, and 1.0% (n = 2, 3, and 4, respectively; Table 2). Upon the major reaction



**Fig. 4.** Kinetics of the change in yield of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H during the interaction of AllOBu with (HMe<sub>2</sub>Si)<sub>2</sub>O in the presence of [Pt–PMS] ( $c_{Pt} = 3 \times 10^{-3}$  mol/L, 120°C). (1) total yield of free siloxane and siloxane bound in the hydrosilylation products; (2) yield of the bound siloxane; and (3) yield of the free siloxane.

(22 h), the yield of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H accounting for their consumption for hydrosilylation was 27.7, 5.9, and 2.2% (n = 2, 3, and 4, respectively). The decrease in the fraction of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>2</sub>H was not proportional to the increase in the amount of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>4</sub>H, likely due to the higher reactivity of the former in comparison to HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>4</sub>H as well as its disproportionation into (HMe<sub>2</sub>Si)<sub>2</sub>O and HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>3</sub>H [8].

Hence, the duration of the induction period and the hydrosilylation itself were the major factors affecting the amount of the side siloxanes and the allyl-propenyl isomerization of the allyl ethers.

The presence of the second Si–H group in the monoadducts allowed their interaction with the allyl ether to form the products of double addition even in the excess of (HMe<sub>2</sub>Si)<sub>2</sub>O. Hydrosilylation of AllOGlyc, due to the ether high reactivity, gave exclusively the  $\gamma$ , $\gamma$ -adduct, its fraction being 17.3% at 120°C. The temperature decrease reduced its amount almost twofold (the  $\gamma$ , $\gamma$ -adduct fraction was 9.5 and 9.0% at 100 and 80°C, respectively).

The yield of the  $\gamma$ , $\gamma$ -addition product during the AllO-Bu interaction with  $(HMe_2Si)_2O$  was lower (13.4%) than for AllOGlyc, yet the products of  $\beta$ , $\beta$ - and  $\beta$ , $\gamma$ -addition were detected (yield <0.8%). The amount of the AllOEt and AllOBn hydrosilylation with the Si–H group of the monoadducts when the major reaction was complete was only slightly different from that in the case of AllOBu (14.2 and 14.8% for AllOEt and AllOBn, respectively), but hydrosilylation of AllOBn gave  $\gamma$ , $\gamma$ - and  $\beta$ , $\gamma$ -adducts, the  $\gamma$ , $\gamma$ -adduct being exclusively formed in the case of AllOEt (Table 1).

The amounts of the products of double addition during AllOPh and AllOGlyc hydrosilylation were comparable, being higher than for other ethers (17.7%). The  $\beta$ , $\gamma$ -adduct yield was 2–3 times higher than for hydrosilylation of AllOBu and AllOBn, whereas the  $\beta$ , $\beta$ -adduct was formed in trace amount.

Hydrosilylation of the allyl ethers with the formed monoadducts bearing free SiH group was much slower than with 1,1,3,3-tetramethyldisiloxane, and the targeted preparation of the double addition products demanded the excess of the allyl ether and considerable reaction duration. The same has been observed for comparative hydrosilylation of aliphatic ethers terephthaloyl bis(4hydroxybenzoates) with 1,1,3,3-tetramethyldisiloxane and 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxane [21].

Selectivity of allyl ethers hydrosilylation is usually regarded as the ratio between the  $\gamma$ - and  $\beta$ -adducts (regioselectivity) disregarding the side reactions. In this study, regioselectivity of (HMe<sub>2</sub>Si)<sub>2</sub>O addition during hydrosilylation of AllOGlyc and AllOEt was close to the maximum—99.0 and 99.7%, respectively ( $c_{\text{Pt}}=3\times10^{-3}$  mol/L, 120°C). The ratio between products of  $\gamma$ - and  $\beta$ -addition of (HMe<sub>2</sub>Si)<sub>2</sub>O during hydrosilylation of AllOBu and AllOBn was close (97.3 and 97.0%, respectively), being lower (92.1%) only for AllOPh.

Selectivity of the reaction [the ratio between the product of γ-addition (HMe<sub>2</sub>Si)<sub>2</sub>O to all the compounds formed from AllOR, including the side reactions products and the products of mono- and bis-addition of the side siloxanes HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (n = 2-4) to AllOR] was lower than the regioselectivity (45.2-60.3% at 120°C) due to the formation of the double addition products and high reactivity of HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (Table 1). It could be suggested that the low selectivity of AllOR hydrosilylation was majorly due to the induction period; however, the selectivity of the AllOGlyc reaction at 120°C was close to that of other ethers despite the shortest induction period, due to side reactions of AllOGlyc and significant formation of the product of the  $\gamma$ , $\gamma$ -addition (60.3%); the decrease in temperature increased the selectivity (65%). As in the case of (HMe<sub>2</sub>Si)<sub>2</sub>O addition, selectivity of the reaction for AllOPh was the lowest among the studied ethers (45.2%).

Total  $\gamma$ -addition ( $\gamma_{\Sigma}$ -selectivity) accounting for the contribution of all the  $\gamma$ -adducts formed during hydrosilylation (including that with side siloxanes and the

products of double addition) in order to extrapolate the obtained data to hydrosilylation with oligomeric and polymeric silicon hydrides (in those cases the disproportionation has practically no effect on the average molecular mass and the properties of the reaction product) was estimated as of 96.1 and 95.3% for AllOBu and AllOEt hydrosilylation, respectively, about 36% higher than the selectivity of  $(HMe_2Si)_2O$  addition.  $\gamma_{\Sigma}$ -Selectivity of AllOGlyc, AllOBn, and AllOPh hydrosilylation was of 86.4, 89.8, and 89.8%, respectively. However, the selectivity in the case of [Pt-PMS] or homogeneous cyclooctadiene (85%), dibenzyl sulfide (87%), and dimethyl sulfoxide (84%) platinum complexes was lower than in the case of the Wilkinson catalyst [Rh(Ph<sub>3</sub>P)<sub>3</sub>Cl] (95%) [14]. The  $\gamma_{\Sigma}$ -selectivities calculated from the GLC and 1H NMR data were in agreement [it was impossible to determine the selectivity of hydrosilylation exclusively of the product of (HMe<sub>2</sub>Si)<sub>2</sub>O γ-addition from the <sup>1</sup>H NMR data due to the overlap of the signals of the products of hydrosilylation with the starting hydrosiloxane and the side hydrides HMe<sub>2</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>H (n = 2, 3)].

The possibility of repeated use is an important feature of the immobilized metal complexes. Platinum(II) immobilized on PMS withstood at least 10 cycles of AllOGlyc hydrosilylation (120°C,  $c_{Pt}$  = 3×10<sup>-3</sup> mol/L); TON<sub>AllOGlyc</sub>> 8550,  $\text{TOF}_{\text{AllOGlyc}} = 3.5683 \text{ s}^{-1}$ ,  $\text{TOF}_{\text{AllOBu}} = 0.9416 \text{ s}^{-1}$ ,  $TOF_{AllOEt} = 0.1283 \text{ s}^{-1}, TOF_{AllOBn} = 0.1121 \text{ s}^{-1}, \text{ and}$  $TOF_{AllOPh} = 0.1022 \text{ s}^{-1}$ . The duration of the catalyst contact with the reaction mixture should have been increased after the 3<sup>rd</sup> cycle to preserve high conversion of the ether (Table 3). The decrease in temperature to 80°C negatively affected the number of productive cycles (due to low activity of the catalyst), coinciding with the data in Refs. [22, 23]. The repeated use of the [Pt-PMS] complex was comparable to silica-immobilized Pt(0) bearing ethylene oxide fragments [24]. The [Pt-PMS] complex withstood four cycles during hydrosilylation of 1,3-divinyl-1,1,3,3tetramethyldisiloxane with 1,1,3,3-tetramethyldisiloxane [5].

Selectivity of the reaction, its regioselectivity and,  $\gamma_{\Sigma}$ -selectivity remained practically unchanged during repeated use of [Pt–PMS] (Table 3); the amount of side products of siloxanes and ethers transformations remained the same as well. Washing of the catalyst with methylene chloride did not affect the reaction selectivity.

To understand the mechanism of catalytic action of [Pt–PMS], we studied the effect of the prior treatment of the catalytic complex with 1,1,3,3-tetramethyldisiloxane

Cycle <i>T</i> , no. °C	<i>Т</i> ,	Time, h	Conversion of	$\gamma_{\Sigma}$ -Selectivity,	γ/β, %	Product of (HMe <sub>2</sub> Si) <sub>2</sub> O addition, %				CH <sub>3</sub> CH=CHOGlyc,	Others,
		AllOGlyc, %	%		β-	γ-	β,γ-	γ,γ-	70	70	
1	80	7.00	92	93.3	92.1/7.9	5.3	62.6	0.0	9.3	5.4	17.4
2	80	7.00	94	92.5	91.0/1.0	6.1	61.6	0.0	10.0	4.9	17.4
3	80	7.00	90	98.8	98.6/1.4	1.0	67.6	0.0	11.8	5.6	14.0
4	80	7.00	59	92.1	90.8/9.2	6.6	65.7	0.0	12.0	6.5	9.2
5	80	7.00	56	92.0	91.7/8.3	5.9	65.0	1.0	11.8	7.7	8.6
6	80	7.00	33	93.1	91.9/8.1	6.2	70.4	0.0	8.6	6.1	8.7
1	120	1.25	99	96.0	95.5/4.5	2.8	58.5	0.0	9.3	5.6	23.8
2	120	1.25	99	96.5	95.8/4.2	2.5	57.6	0.7	12.7	5.7	20.7
3	120	1.25	94	95.8	96.3/3.7	2.1	53.0	0.8	17.1	6.1	20.8
4	120	1.25	84	94.9	94.4/5.6	3.3	55.6	1.3	12.5	5.8	21.6
	120	2.00	99	96.0	94.8/5.2	3.6	66.0	0.0	15.0	3.7	11.7
5	120	2.50	97	95.5	93.9/6.1	4.1	63.5	0.0	18.7	3.4	10.3
6	120	2.50	97	96.7	94.8/5.2	2.9	53.1	0.0	26.0	5.0	13.0
7	120	3.00	94	96.9	93.4/6.6	2.7	38.6	0.0	40.7	5.2	12.8
8	120	6.00	92	96.0	93.7/6.3	3.6	53.0	0.0	26.7	5.3	11.5
9	120	7.50	96	95.5	93.1/6.9	4.0	54.1	0.0	23.1	5.1	13.7
10	120	7.50	95	95.0	92.8/7.2	4.4	56.1	0.0	18.7	3.8	17.0

Table 3. Repeated using of [Pt–PMS] in hydrosilylation of allyl glycidyl ether with 1,1,3,3-tetramethyldisiloxane<sup>a</sup>

<sup>a</sup>  $c_{\text{Pt}} = 3 \times 10^{-3} \text{ mol/L}$ , ether : siloxane molar ratio = 1 : 1.5.

or AllOGlyc (2 h, 80°C) followed by hydrosilylation on the obtained interaction product. The pre-activation of [Pt–PMS] with 1,1,3,3-tetramethyldisiloxane was accompanied by the change in the solution color from colorless to yellow-green, typical of the formation of platinum-silicon hydride complexes [25].

IR spectrum of the specimen obtained via the treatment with 1,1,3,3-tetramethyldisiloxane and washing of the complex with  $CH_2Cl_2$  contained two bands of the siloxane methyl groups at 804 and 1259 cm<sup>-1</sup>, and a new band appearing at 1093 cm<sup>-1</sup> could be assigned to the v<sub>as</sub>(Si–O–Si) stretching, the v(Si–H) signal at 2300– 2400 cm<sup>-1</sup> being absent. The change in the IR spectrum of [Pt–PMS] upon the treatment with 1,1,3,3-tetramethyldisiloxane were likely due to the oxidative addition of the silicon hydride to form the Pt–Si bond [25, 26].

Catalytic activity of [Pt–PMS] upon the treatment with 1,1,3,3-tetramethyldisiloxane and addition of

AllOGlyc at room temperature (18-25°C) was comparable to that of the starting [Pt-PMS], however, if the addition of AllOGlyc upon the treatment was performed at higher temperature (30-40°C), conversion of the ether (80% after 2 h at 80°C) was significantly increased in comparison with simultaneous addition of the reactants (29%). A similar trend of the increase in alkene conversion via pre-activation of homogeneous *cis*-[Pt(Me<sub>2</sub>SO)<sub>2</sub>Cl<sub>2</sub>], cis-[Pt(Et<sub>2</sub>SO)<sub>2</sub>Cl<sub>2</sub>], and [Pt(MeCOD)Cl<sub>2</sub>] catalysts with 1,1,3,3-tetramethyldisiloxane has been observed during hydrosilylation of  $\alpha$ -methylstyrene [27], suggesting the common mechanism. Pre-activation of [Pt-PMS] with 1,1,3,3-tetramethyldisiloxane positively affected the selectivity of hydrosilylation: the amount of the products of (HMe<sub>2</sub>Si)<sub>2</sub>O y-addition to AllOGlyc was increased (the  $\gamma/\beta$ -adducts ratio being 92.8/7.2); the hydrosilylation selectivity was up by 5.8%, the  $\gamma_{\Sigma}\text{-selectivity}$  was up by 1.2%; the amounts of the products of side transformations of AllOGlyc was decreased (the fraction of the propenyl and propyl glycidyl ethers being 3.3 and 3.2%, respectively).

The pre-treatment of [Pt–PMS] with AllOGlyc deactivated the complex. Further addition of the siloxane to the so treated sample led to the ether conversion as low as 2% after 2 h at 80°C, probably due to the formation of an inefficient  $\pi$ -allyl complex; however, the IR spectrum of the catalyst was not changed upon the treatment with AllOGlyc. Pre-activation of homogeneous sulfurcontaining complexes, *cis*-[Pt(Me<sub>2</sub>SO)<sub>2</sub>Cl<sub>2</sub>] and *cis*-[Pt(Et<sub>2</sub>SO)<sub>2</sub>Cl<sub>2</sub>], has significantly decelerated the hydrosilylation of  $\alpha$ -methylstyrene as well [27].

Analysis of the obtained data in view of earlier studies [3, 5] and the existing concepts of the hydrosilylation mechanism suggested that the key stage of the reaction was the primary interaction of [Pt–PMS] with (HMe<sub>2</sub>Si)<sub>2</sub>O. Subsequent attack of the allyl group affording the corresponding intermediate (introduction at the Pt–Si bond) led to hydrosilylation, whereas other transformations of the silicon complex of platinum activated the side processes involving hydrosiloxanes. The intermediate formation was affected by the siloxane and allyl ether structure and led to the induction period observed for certain systems. In its turn, primary coordination of the allyl ether was the major reason for isomerization of its double bond or the reduction upon the attack of the intermediate with hydrosiloxane.

#### EXPERIMENTAL

1,1,3,3-Tetramethyldisiloxane and allyl glycidyl ether (Acros), allyl butyl, allyl phenyl, and allyl benzyl ethers (Aldrich), allyl ethyl ether (Fluka), and toluene and methylene chloride ("analytical pure" grade) were used. The [Pt–PMS] complex was obtained as described elsewhere [5].

Chromatographic analysis of the hydrosilylation products was performed using an Agilent 7890A chromatograph equipped with a heat conductivity detector. Other conditions were as follows: capillary column DB-1 (30 m×0.32 mm, phase film thickness 1  $\mu$ m), specimen volume 0.5  $\mu$ L, evaporator temperature 250°C; for the reaction mixtures based on AllOPh and AllOBn: column temperature 150°C (4 min), heating to 290°C at 42 deg/min, 35 min at 290°C, carrier gas: helium with 1 : 300 splitting; for the reaction mixtures based on AllOEt, AllOBu, and AllOGlyc: column temperature 70°C (5 min), heating to 200°C at 5 deg/min, heating to 225°C at 25 deg/min, 45 min at 225°C, carrier gas: helium with 1 : 250 splitting.

IR spectra were recorded using a Shimadzu FTIR-8400S spectrometer (4000–400 cm<sup>-1</sup>) in KBr pellets.

**Hydrosilylation of allyl ethers** was performed in ampoules at 80–120°C. Weighed amount of the catalyst was charged into an ampoule, and a mixture of the siloxane, allyl ether, and toluene (molar ratio 6 : 4 : 1 was added); platinum concentration in the reaction mixture was  $3\times10^{-4}$ – $3\times10^{-3}$  mol/L at  $c_{\text{Pt}} = 8\times10^{-5}$  mol/g with respect to the carrier. Conversion and selectivity were determined by means of GLC (kinetic method) using toluene as internal reference as described elsewhere [3].

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## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

#### REFERENCES

- Advances in Silicon Science, Marciniec, B., Ed., London: Springer, 2009, vol. 1, p. 32. https://doi.org/10.1007/978-1-4020-8172-9
- de Vekki, D.A., Il'ina, M.A., and Skvortsov, N.K., *Izv. SpbGTI(TU)*, 2015, no. 32(58), p. 54. https://doi.org/10.15217/issn998984-9.2015.32.54.
- de Vekki, D.A., Il'ina, M.A., and Skvortsov, N.K., *Russ.* J. Gen. Chem., 2018, vol. 88, no. 1, p. 25. https://doi.org/10.1134/S107036321801005X
- 4. Gafiatullin, R.R., *Candidate Sci. (Tech.) Dissertation*, Priyutovo, 2000.
- de Vekki, D.A., Kuchaev, E.A., Afonin, M.V., and Simanova, S.A., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 4, p. 575. https://doi.org/10.1134/S1070363208040105
- Il'ina, M.A., Mashlyakovskii, L.N., Drinberg A.S, Khomko, E.V., and Garabadzhiu, A.V., *Russ. J. Appl. Chem.*, 2019, vol. 92, no. 4, p. 530. https://doi.org/10.1134/S0044461819040091
- Chrusciel, J.J. and Lesniak, E., *Prog. Polym. Sci.*, 2015, vol. 41, p. 67. https://doi.org/10.1016/j.progpolymsci.2014.08.001
- 8. Il'ina, M.A., de Vekki, D.A., and Skvortsov, N.K., Russ.

*J. Gen. Chem.*, 2014, vol. 84, no. 1, p. 40. https://doi.org/10.1134/S1070363214010095

- Safa, K.D., Bahadori, A., Tofangdarzadeh, S., and Nasirtabrizi, M.H., *J. Iran. Chem. Soc.*, 2008, vol. 5, no. 1, p. 37. https://doi.org/10.1007/BF03245813
- Chernyshev, E.A., Belyakova, Z.V., Knyazeva, L.K., and Khromykh, N.N., *Russ. J. Gen. Chem.*, 2007, vol. 77, no. 1, p. 55. https://doi.org/10.1134/S1070363207010082
- Marciniec, B., Walczuc, E., Blazejewska-Chadyniak, P., Kujawa-Welten, M., and Krompiec, S., *Organosilicon Chem.*, 2003, p. 415. https://doi.org/10.1002/9783527619924.ch67
- Belyakova, Z.V., Pomerantseva, M.G., Efimova, L.A., Chernyshev, E.A., and Storozhenko, P.A., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 4, p. 728. https://doi.org/10.1134/S1070363210040079
- Feng, S. and Cui, M., *React. Funct. Polym.*, 2000, vol. 45, no. 2, p. 79. https://doi.org/10.1016/S1381-5148(00)00013-4
- Andreev, S.A., Il'ina, M.A., Volkova, A.M., de Vekki, D.A., and Skvortsov, N.K., *Russ. J. Appl. Chem.*, 2010, vol. 83, no. 11, p. 1962. https://doi.org/10.1134/S1070427210110133
- de Vekki, D.A. and Skvortsov, N.K., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 4, p. 598. https://doi.org/10.1134/S107036320904015X
- Wang, W., *Eur. Polym. J.*, 2003, vol. 39, no. 6, p. 1117. https://doi.org/10.1016/S0014-3057(02)00374-9
- 17. Schilling, C.L., J. Organomet. Chem., 1971, vol. 29, no. 1,

p. 93.

- 18. Comprehensive Handbook on Hydrosilylation, Marciniec, B., Ed., Oxford: Pergamon Press, 1992.
- Andrianov, K.A., Souček, J., and Khananashvili, L.M., *Russ. Chem. Rev.*, 1979, vol. 48, no. 7, p. 657. https://doi.org/10.1070/RC1979v048n07ABEH002390
- 20. Zuev, V.V. and de Vekki, D.A., *Russ. J. Org. Chem.*, 2006, vol. 42, no. 8, p. 1108. https://doi.org/10.1134/S107042800608001X
- Rozga-Wijas, K., Chojnowski, J., Fortuniak, W., Scibiorek, M., Michalska, Z., and Rogalski, L., *J. Mater. Chem.*, 2003, vol. 13, p. 2301. https://doi.org/10.1039/B304134D
- 22. Marciniec, B., Maciejewski, H., Szubert, K., and Kurdykowska, M., *Monatsh. Chem.*, 2006, vol. 137, no. 5, p. 605.

https://doi.org/10.1007/s00706-006-0461-9

- Maciejewski, H., Szubert, K., Marciniec, B., and Pernak, J., *Green Chem.*, 2009, vol. 11, no. 7, p. 1045. https://doi.org/10.1039/b819310j
- 24. Alauzun, J., Mehdi, A., Reye, C., and Corriu, R., *Chem. Matter.*, 2007, vol., 19, no. 26, p. 6373. https://doi.org/10.1021/cm7019087
- Huang, J., Liu Zh., Liu, X., He Ch., Chow Sh.Y., and Pan, J., *Langmuir*, 2005, vol. 21, no. 2, p. 699. https://doi.org/10.1021/la0482148
- 26. Stein, J., Lewis, L.N., Gao, Y., and Scott, R.A., J. Am. Chem. Soc., 1999, vol. 121, no. 15, p. 3693. https://doi.org/10.1021/ja9825377
- 27. Petrenko, M.Yu., de Vekki, D.A., and Skvortsov, N.K., *Izv. SpbGTI(TU)*, 2009, no. 5(31), p. 53.