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Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV, Kh. M. MINACHEV, V. A. PONOMARENKO, B. A. SOKOLOV, and G. V. ODABASHYAN

STUDY OF CERTAIN GROUP VIII METALS AS CATALYSTS IN THE REACTION OF ADDITION OF $RSiHCl_2$ TO UNSATURATED COMPOUNDS

In recent reports ([1−3]) the possibility was demonstrated of successfully using platinized carbon in the reaction of addition of silane hydrides to unsaturated compounds. The suitability of platinized carbon for carrying out the indicated reactions—in place of the peroxides, ultraviolet light, $AlCl_3$, $ZnCl_2$, BCl_3, etc., usually used for these purposes—opens a new field of activity for investigators. In this connection, it was of interest to study the possibility of using other heterogeneous hydrogenating and dehydrogenating catalysts for carrying out similar reactions. In the present work we examined the catalytic action of a series of metals of the eighth group, using as an example the reaction of addition of ethyldichlorosilane to allyl chloride:

$$C_2H_5SiHCl_2 + CH_2{=}CH{-}CH_2Cl \rightarrow C_2H_5Si(Cl)_2CH_2CH_2CH_2Cl \qquad (1)$$

The choice of precisely this reaction is due to two reasons. On the one hand, the reaction of addition of ethyldichlorosilane to allyl chloride leads to the production of an organosilicon compound with chlorine in the γ-position to Si and, on the other hand, this reaction has been studied by us in sufficient detail ([2,3]) using the example of the catalytic action of platinized carbon. As was shown, in this case, along with the main addition reaction according to scheme (1), the formation of by-products took place: ethyltrichlorosilane ($C_2H_5SiCl_3$) and ethylpropyldichlorosilane ($C_2H_5Si(Cl)_2C_3H_7$).

In studying the possibility of using other metals of the eighth group for the above-mentioned reaction, we set ourselves the following tasks: 1) to determine the influence of the chemical nature of the support on the extent of the main reaction (according to scheme 1), and 2) to reveal differences in the behavior of various metals and the degree of generality of their action on the course of both the main and side reactions, all other conditions being equal. We used the following catalysts: 0.5% $Pt—SiO_2$, 1% $Pt—Al_2O_3$, 1% $Ru—Al_2O_3$, 1% $Rh—Al_2O_3$, 5% $NiNO_3—C^*$, 0.5% $Pd—SiO_2$, 2% $Pd—Al_2O_3$, 1% $Ru—SiO_2$, 0.5% Rh—SiO_2, 5% Ni—C*, and 5% Co—C*. All of them were prepared under standard conditions—by impregnating the supports with dilute solutions of H_2PtCl_6, $PdCl_2$, H_3RhCl_6, $(NH_4)_2RuCl_5NO$, $Ni(NO_3)_2$, and $Co(NO_3)_2$ at room temperature. The catalysts prepared in this way were dried at 110—115° for 4-5 hr, then placed in a glass tube of an electric furnace and reduced with electrolytic hydrogen with a gradual increase of the temperature to 340—350°. In all, the reduction lasted 10-12 hr. The specific surface area** of the catalysts Pt—Al_2O_3, Rh—Al_2O_3, Ru—Al_2O_3, and Pd—Al_2O_3 was 70-85 m^2/g, and in the case of deposition of these same metals on SiO_2, 220 m^2/g. In the catalysts Pt—C, Ni—C, and Co—C the surface area was not determined.

* Activated birch charcoal.

** The specific surface area of the catalysts was determined from benzene adsorption isotherms at 0°.

The addition reaction of $C_2H_5SiHCl_2$ to $CH_2 = CHCH_2Cl$ with all catalysts was carried out under standard conditions: a molar ratio of $C_2H_5SiHCl_2$ to allyl chloride of 1 : 1 (129 and 77 g, respectively), 6-hour heating in a rotating autoclave at 160°. Distillation of the reaction products after filtration of the catalyst was carried out on a column with 35-40 theoretical plates. Before being charged into the autoclave, the catalyst was ground. Ethyldichlorosilane and allyl chloride were introduced into the reaction freshly distilled.

The experimental data obtained with different catalysts are summarized in Table 1. Consideration of the data presented therein makes it possible to divide the catalysts studied into two groups: A—catalysts that promote the course of the main addition reaction (scheme 1), which include catalysts 1-4; B—catalysts that promote side reactions leading to the formation of $C_2H_5SiCl_3$ and $C_2H_5Si(Cl)_2C_3H_7$ (catalysts 5-8).

Table 1

Experimental data obtained in the interaction of $C_2H_5SiHCl_2$ with $CH_2 = CHCH_2Cl$ on various catalysts

No.	Catalyst	Catalyst weight, g	Max. pressure at 160°, atm	Pressure at room temp. after reaction, atm	Weight of liquid reaction products, g	$CH_2=CHCH_2Cl$, g	$C_2H_5SiH_2Cl$, g	$C_2H_5SiHCl_2$, g	$C_2H_5SiCl_3$, g	$C_2H_5Si(Cl)_2 \cdot CH_2CH_2CH_2Cl$, g	$C_2H_5Si(Cl)_2 \cdot CH_2CH_2CH_2Cl$, % of theory
1	1% Pt on carbon	0,3	14	0,0	193	7,5	–	43,4	18,6	100	48,8
2	0,5% Pt on SiO_2	0,6	12	1,0	201	11,2	–	38,4	21,7	104	50,7
3	1% Pt on Al_2O_3	0,3	12	0,0	199	9,4	–	43,5	23,8	102,7	50,0
4	1% Ru on Al_2O_3	0,3	14	1,5	193	18,7	23	36,0	11,3	80,5	39,4
5	1% Rh on Al_2O_3	0,3	32	7,0	167	traces	–	119	6,2	11,8	5,7
6	5% $NiNO_3$ on carbon	0,3	32	6,0	172	traces	11	111	8,2	traces	–
7	0,5% Pd on SiO_2	0,6	35	6,0	170	traces	–	124	8,2	4,7	2,3
8	2% Pd on Al_2O_3	0,3	40	8,0	160	traces	–	136	–	–	–

No.	Catalyst	Catalyst weight, g	Max. pressure at 160°, atm	Pressure at room temp. after reaction, atm	Weight of liquid reaction products, g	$CH_2=CHCH_2Cl$, g	$C_2H_5SiHCl_2$, g	$C_2H_5SiCl_3$, g	$C_2H_5Si(Cl)_2C_3H_7$, g	$C_2H_5Si(Cl)_2 \cdot CH_2CH_2CH_2Cl$, g	$C_2H_5Si(Cl)_2 \cdot CH_2CH_2CH_2Cl$, % of theory
19	1% Ru on SiO_2	0,3	14	0,0	201	51,6	70	7,4	traces	traces	–
10	0,5% Rh on SiO_2	0,6	17	0,5	197	47,8	89	17,8	traces	traces	–
11	5% Ni on carbon	0,3	14	0,0	198	67,5	98,4	–	–	–	–
12	5% Co on carbon	0,3	21	0,0	202	46,9	109,2	traces	traces	–	–

Let us consider each group separately.

Catalysts of group A. First of all, it should be noted that all platinum catalysts are active; although they cause, to some extent, side reactions involving the formation of $C_2H_5SiCl_3$ and $C_2H_5Si(Cl)_2C_3H_7$, they nevertheless give the highest yield of addition products. It is of interest that neither the concentration of the metal nor the nature of the support affected the ratio and amount of all the reaction products formed. Close to the platinum catalysts is 1% Ru on Al_2O_3. True, in this case a significantly larger portion of the starting substances did not enter into reaction. The possibility of using Ru in this reaction had not previously been noted by anyone. From a preparative point of view, it is also important that, instead of carbon, when platinum is used one may employ Al_2O_3 and silica gel.

Catalysts of group B. 1% Rh on Al_2O_3, 5% $NiNO_3$ on carbon, and 0,5% Pd on SiO_2 catalyze the addition reaction (according to scheme 1) to a very slight extent. At the same time, on the indicated catalysts and

$C_2H_5Si(Cl)_2C_3H_7$ is also formed in small amounts. On these catalysts, however, the principal process is the formation of ethyltrichlorosilane and gaseous products, accompanied by an increase in pressure to 32–40 atm. This is especially pronounced in the case of 2% Pd on Al_2O_3 (8).

It is seen from Table 1 that a series of metals on SiO_2 and activated carbon (9–12) exerted no catalytic action at all. It is not entirely clear why such metals as Ru and Rh, which catalyzed reactions in groups A and B, prove inactive when deposited on SiO_2.

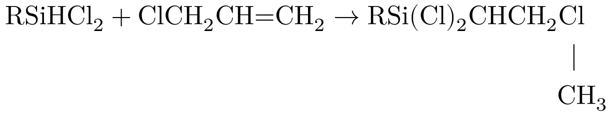
The reaction between silane hydrides of the type $RSiHCl_2$ and allyl chloride on catalysts of group A proceeds practically to completion within 10–15 min. Thus, CH_3SiHCl_2 and $CH_2{=}CHCH_2Cl$ in the presence of 1% Pt-C, with only one rapid heating to 160°, give addition products in high yield. The character of the distillation curves after short-term and after prolonged heating is almost identical. A particularly noticeable increase in pressure, accompanied by a more rapid rise in temperature, is observed at 100–120°.

In conclusion let us consider the side reactions of formation of $C_2H_5SiCl_3$ and $C_2H_5Si(Cl)_2C_3H_7$. The following routes for the formation of these compounds are possible:

1. a) $RSiHCl_2 + ClCH_2CH{=}CH_2 \rightarrow RSiCl_3 + CH_3CH{=}CH_2$

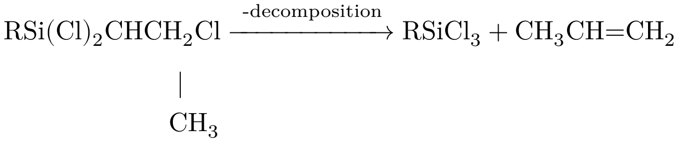
   b) $CH_3CH{=}CH_2 + RSiHCl_2 \rightarrow RSi(Cl)_2C_3H_7$

2. a)



$$RSiHCl_2 + ClCH_2CH{=}CH_2 \rightarrow RSi(Cl)_2\underset{\substack{|\\ CH_3}}{CH}CH_2Cl$$

b)



$$RSi(Cl)_2\underset{\substack{|\\ CH_3}}{CH}CH_2Cl \xrightarrow{\text{-decomposition}} RSiCl_3 + CH_3CH{=}CH_2$$

c) see 1, b

3. $2RSiHCl_2 \xrightarrow[\text{heating}]{\text{Pt–C}} RSiCl_3 + RSiH_2Cl$

4. $RSiHCl_2 + ClCH_2CH_2CH_2Si(Cl)_2R \xrightarrow[\text{heating}]{\text{Pt–C}} RSiCl_3 + RSi(Cl)_2C_3H_7$

or $ClCH_2CHSi(Cl)_2R$

|

CH_3 $R = C_2H_5$

An experimental check of schemes 3 and 4 under our standard conditions did not lead to the formation of $C_2H_5SiCl_3$ and $C_2H_5Si(Cl)_2C_3H_7$. Scheme 2 is probable; however, it is difficult to suppose that catalysts of group B, in contrast to catalysts of group A, promoted the addition (and in the fully reversed sense) of allyl chloride and at the same time did not facilitate the addition of propylene. The most probable scheme, therefore, proves to be scheme 1.

Thus, the addition of ethyldichlorosilane to allyl chloride proceeds with equal yields on the catalysts–1% Pt on carbon, 0.5% Pt on SiO_2, and 1% Pt on Al_2O_3. 1% Ru on Al_2O_3 gives a somewhat lower yield of addition products. Other catalysts (1% Rh on Al_2O_3, 0.5% Pd on SiO_2, and 5% $NiNO_3$ on carbon), while promoting addition reactions only to an insignificant extent, mainly facilitate the reaction of replacement in ethyldichlorosilane of hydrogen at Si by chlorine, which proceeds most readily in the case of 2% Pd on Al_2O_3.

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Note: Figure translations are in progress. See original paper for figures.

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