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Abstract

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ON THE MECHANISM OF THE ADDITION REACTION OF SILICON HYDRIDES TO UNSATURATED COMPOUNDS IN THE PRESENCE OF PLATINIZED CARBON AND CHLOROPLATINIC ACID

Regarding the mechanism of the addition reaction of silicon hydrides to unsaturated compounds in the presence of platinized carbon and chloroplatinic acid, Benkeser and Hickner ([1]), Speier and co-workers ([2,3]), Goodman, Silverstein, and Benitez ([4]) have suggested that it proceeds by a heterolytic, ionic mechanism.

Our observations on the "competitive" addition of silicon hydrides to fluoroethyl allyl ethers, on the contrary, led us to the conclusion that it is rather a specific homolytic reaction ([5,6]). Its specificity consists in the fact that it proceeds on the surface of a heterogeneous catalyst. The possibility of radical reactions of this kind in heterogeneous catalysis has now been substantiated both theoretically ([7,8]) and experimentally ([9]).

In the present work we continued the study of the mechanism of the addition reaction of silicon hydrides to unsaturated compounds in the presence of platinized carbon. First of all, we attempted to "trap" the radicals arising upon the interaction of silicon hydrides with platinized carbon and evidently associated with it, using diphenylpicrylhydrazyl. The data in Table 1 convincingly show that the catalyst considerably facilitates the homolytic cleavage of Si–H bonds in $C_6H_5SiH_3$, $(C_6H_5)_2SiH_2$, $(C_6H_5)_3SiH$, $(C_2H_5)_3SiH$, and $(CH_3)_2(C_2H_5)_2SiH$, leading to the formation of atomic hydrogen, which is "trapped" by diphenylpicrylhydrazyl

$$\equiv \mathrm{Si{-}H} \xrightarrow[\sim 90-95^\circ]{\mathrm{Pt/C}} \equiv \dot{\mathrm{S}}\mathrm{i} + \dot{\mathrm{H}} \xrightarrow{(\mathrm{C_6H_5})_2\dot{\mathrm{N}}\mathrm{NC_6H_2(NO_2)_3}} \equiv \dot{\mathrm{S}}\mathrm{i} + (\mathrm{C_6H_5})_2\mathrm{NNHC_6H_2(NO_2)_3}.$$

That no hydrogenation of the NO_2 groups occurs in this process is proved by the reverse conversion of diphenylpicrylhydrazine into the free radical diphenylpicrylhydrazyl, which is readily effected under the influence of lead dioxide

$$(C_6H_5)_2NNHC_6H_2(NO_2)_3 \xrightarrow{PbO_2} (C_6H_5)_2\dot{N}NC_6H_2(NO_2)_3.$$

The rate of cleavage of the Si—H bond, as is seen from Table 1, depends substantially on the structure of the silicon hydride: the more shielded by substituents the reacting Si—H bond is, the more difficult the cleavage. In the case of $(C_6H_5)_3SiH$, under the standard conditions we selected, homolytic hydrogenation of diphenylpicrylhydrazyl is almost not observed. Toluene and tetrafluoroethyl allyl ether, either without catalyst or in its presence, do not cause the formation of radicals that could be "captured" by diphenylpicrylhydrazyl.

As we have already reported ([6]), in "competitive" addition the silicon hydrides we used are arranged in the following series of decreasing activity:

$$(CH_3)(\underset{2,5}{C_2H_5})_2SiH > (CH_3)(\underset{1,2}{C_2H_5})(Cl)SiH > (\underset{1}{C_2H_5})(Cl)_2SiH > \underset{0,9}{Cl_3SiH}$$

whereas in ordinary addition they are arranged in a somewhat different order:

$$(C_2H_5)(Cl)_2SiH > (CH_3)(C_2H_5)(Cl)SiH > Cl_3SiH > (CH_3)(C_2H_5)_2SiH.$$

The addition of even small amounts of $C_2H_5SiHCl_2$ to $(CH_3)(C_2H_5)_2SiH$ substantially facilitates the addition of the latter.

Table 1

Homolytic hydrogenation of diphenylpicrylhydrazyl (I)

Experiment no.	Silicon hydride formula	Amount, (moles)	Amount of I, g	Amount of 1% Pt/C, g	Time for conversion of I to II, min
1	$(CH_3)(C_2H_5)_2SiH$	2,04(0,02)	2,04(0,005)	0,0050	240*
2	$(C_2H_5)_3SiH$	2,32(0,02)	2,32(0,005)	0,0050	10040
3	$C_6H_5SiH_3$	2,16(0,02)	2,16(0,005)	0,0050	402
4	$(C_6H_5)_2SiH_2$	3,70(0,02)	3,70(0,005)	0,0050	2010
5	$(C_6H_5)_3SiH$	2,50(0,01)	2,50(0,005)	0,0025	240**
6	$CH_2=CHCH_2OCF_2CF_2H$	3,40(0,02)	3,40(0,005)	0,0050	240**

Experiment no.	Silicon hydride formula	Amount, (moles)	Amount of I, g	Amount of 1% Pt/C, g	Time for conversion of I to II, min
7	$C_6H_5CH_3$	1,85(0,02)	1,85(0,02)	0,0050	960**

* At the boiling temperature of the hydride, 78°.
** During the indicated time no noticeable changes in I are observed.

These facts can be explained by assuming the following radical process on the surface of platinized carbon, beginning with cleavage of the Si—H bond in $C_2H_5(Cl)_2SiH$, which evidently is better adsorbed on the surface:

1. $C_2H_5SiHCl_2 \xrightarrow{Pt/C} C_2H_5\dot{S}iCl_2 + \dot{H}$;
2. $C_2H_5\dot{S}iCl_2 + HSi(CH_3)(C_2H_5)_2 \rightarrow C_2H_5SiHCl_2 + \dot{S}i(CH_3)(C_2H_5)_2$;
3. $(C_2H_5)_2(CH_3)\dot{S}i + CH_2{=}CH \cdot R \rightarrow (C_2H_5)_2(CH_3)SiCH_2\dot{C}HR$;
4. a) $(C_2H_5)_2(CH_3)SiCH_2\dot{C}HR + HSi(CH_3)(C_2H_5)_2 \rightarrow (C_2H_5)_2(CH_3)SiCH_2CH_2R + \dot{S}i(CH_3)(C_2H_5)_2$, etc., or
   b) $(C_2H_5)_2(CH_3)SiCH_2\dot{C}HR + \dot{H} \rightarrow (C_2H_5)_2(CH_3)SiCH_2CH_2R$.

The beginning of the reaction can also be represented in a somewhat different way, namely by addition of the $(C_2H_5)(Cl)_2\dot{S}i$ radical to the multiple bond, followed by involvement in the reaction of $(CH_3)(C_2H_5)_2SiH$, whose Si—H bond is cleaved under the influence of the $(C_2H_5)_2(CH_3)SiCH_2\dot{C}HR$ radical more readily than that in $C_2H_5(Cl)_2SiH$.

The first scheme directly indicates the possibility of deuterium exchange under the influence of platinized carbon between $(C_2H_5)(Cl)_2SiH$ and $(CH_3)(C_2H_5)_2SiD$ under the reaction conditions.

The data of Table 2, which presents the results of experiments on deuterium exchange, confirm this assumption. In the absence of a catalyst there is no deuterium exchange. The catalyst and the walls of the autoclave, on which platinum is always deposited in experiments with H_2PtCl_6, readily bring about deuterium exchange. In this case $C_2H_5SiHCl_2$ enters into the deuterium-exchange reaction by approximately 50%. Consideration of the addition reaction primarily as a homolytic one makes it possible not only to explain a number of previously difficult-to-explain facts, but also

Table 2

Deuterium exchange between $C_2H_5SiHCl_2$ and $(CH_3)(C_2H_5)_2SiD$
(figures in parentheses refer to the product that was in contact with the walls of the autoclave)

Experiment no.	Name of experiment	Amount, 1% Pt/C, g	T_{max}, °C	P_{max}, atm	Reaction duration, h	$C_2H_5SiHCl_2$	$(CH_3)_2SiHCl$	$(C_2H_5)_2SiHCl$	$(CH_3)(C_2H_5)SiHCl$	$C_2H_5SiDCl_2$
1	Heating in a glass ampoule without catalyst	–	153	6	2	59 (30)	10 (22-25)	31 (a)	–(b)	
2	Heating in an autoclave with catalyst	0.2	168	9	2	(30)	(22-25)	(a)	(b)	
3	Heating in a glass ampoule with catalyst	0.05	168	7	2	30	22-25	a	b	

Note. a) The intensity of the Si–D line in $(CH_3)(C_2H_5)_2SiD$–1527 cm^{-1}, according to the IR spectra, decreases considerably; b) a new intense line appears in the IR spectrum at 1608 cm, corresponding to the Si–D frequency in $C_2H_5SiDCl_2$.

to approach the selection of catalysts for this practically important reaction in a somewhat more conscious way. Thus, it is well known that, when silicon hydrides are added to acrylonitrile in the presence of free-radical initiators, the latter readily polymerizes or gives a mixture of high-boiling telomers. In the

presence of platinized carbon, where the process is localized on the catalyst surface, these reactions are suppressed to a considerable extent, but nevertheless do take place. It may be assumed that, in a heterolytic mechanism, these factors will no longer play such a role. It is not by chance that, with acrylonitrile, bases are precisely the most suitable catalysts for addition according to the scheme ([10],[11]):

$$\equiv \mathrm{Si{-}H} + \mathrm{CH_2} = \mathrm{CH_2CN} \rightarrow \equiv \mathrm{SiCH_2CH_2CN}$$

In accordance with these considerations, we carried out the addition of trichlorosilane to acrylonitrile under the influence of dimethylcyanamide, and it proceeded successfully. Dimethylcyanamide is a new catalyst for the addition of silicon hydrides to unsaturated compounds.

Addition in the presence of H_2PtCl_6 undoubtedly proceeds in a more complicated manner, if only because under these conditions H_2PtCl_6 is for the most part reduced to Pt. We believe that in this case as well the homolytic mechanism explains the experimental facts better than the heterolytic one.

Experimental Section

1. Homolytic hydrogenation of diphenylpicrylhydrazyl (I) to diphenylpicrylhydrazine (II). Experiments were carried out under standard conditions at a temperature of 94°, both without a catalyst and in its presence. The results of the experiments are presented in Table 1.

2. **Methyldiethylsilane deuteride** ($CH_3(C_2H_5)_2SiD$).
   80 g (0.58 mole) of methyldiethylchlorosilane, 40 g (4.4 mole) of lithium deuteride, and 105 ml of abs. dibutyl ether were heated for 20 h in a stainless-steel reactor equipped with a mechanical stirrer, thermometer, and rectifying column with a Nichrome packing, at the boiling temperature of the mixture and with vigorous stirring. From the resulting crude mixture of methyldiethylsilane deuteride, repeated rectification gave 30 g (50%) of methyldiethylsilane deuteride, which, according to Raman spectra, contained about 24% $(CH_3)(C_2H_5)_2SiH$, b.p. 76.8° (735 mm), d_4^{20} 0.7102, n_D^{20} 1.3975.

3. **Deuterium exchange between** $C_2H_5SiHCl_2$ **and** $(CH_3)(C_2H_5)_2SiD$**.**
   The influence of the catalyst (1% Pt/C) on deuterium exchange is evident from the data in Table 2. The experiments were carried out in a glass ampoule placed in a stainless-steel autoclave of grade 1X18H9T steel*. To determine the influence of the autoclave walls on deuterium exchange, an experiment was also carried out in the autoclave itself. The conditions of the deuterium-exchange reaction correspond to the conditions of the addition reaction of these same hydrides and deuterides to unsaturated compounds in the presence of 1% Pt/C. Quantitative and qualitative analysis of the mixture of reaction products was carried out by means

of Raman spectra and IR spectra**. The accuracy of determining the content of the components of the mixture is ~ 1–3%. The initial equimolar mixture contained 56% $C_2H_5SiHCl_2$ and 44% $(CH_3)(C_2H_5)_2SiD$ and $(CH_3)(C_2H_5)_2SiH$. According to IR spectra, the content of components in the same mixture was: 59% $C_2H_5SiHCl_2$, 31% $(CH_3)(C_2H_5)_2SiD$, and 10% $(CH_3)(C_2H_5)_2SiH$. For the reaction, 11-46 g of the equimolar mixture and the corresponding amount of catalyst were taken (0.1 g of 1% Pt/C per 0.2 mole of mixture). Comparison of experiments 1 and 3 clearly indicates that 1% Pt/C, under the conditions used for additions, catalyzes deuterium exchange between $C_2H_5SiHCl_2$ and $(C_2H_5)_2(CH_3)SiD$. In this process $C_2H_5SiHCl_2$ enters into the reaction by approximately 50%. The influence of the autoclave walls, on which traces of platinum from experiments with H_2PtCl_6 were deposited, as is seen from experiment 1, is the same as the influence of 1% platinized charcoal.

4. **β-Trichlorosilylpropionitrile** $-Cl_3SiCH_2CH_2CN$.
   40.6 g (0.3 mole) of silicochloroform, 15.5 g (0.3 mole) of acrylonitrile, and 3 g (0.043 mole) of dimethylcyanamide in a glass vessel placed in a test-tube autoclave were gradually heated over 2 h. At 124° a temperature jump to 168° was observed, and the pressure reached 8 atm. From the crude mixture of reaction products, after two distillations in vacuum, 20.3 g (37%) of pure β-trichlorosilylpropionitrile was isolated, b.p. 92-94° (15 mm), m.p. 34-35°. Literature data ([12]): m.p. 32-33°.

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* The indicated steel grade contains, in percent: C ~0.08, Mn ~1.22, Si ~0.34, P ~0.026, S ~0.01, Cr ~17.45, Ni ~10.43, Ti ~0.42.

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