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Abstract

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ON THE POSSIBILITY OF CATALYTIC DEHYDROGENATION OF SILICON HYDROCARBONS

(Presented by Academician A. V. Topchiev on 5 VIII 1957)

There are no reports in the literature on the possibility of catalytic dehydrogenation of silicon paraffins. B. N. Dolgov, G. V. Golodnikov, and N. E. Glushkova, studying the transformations of tetraethylsilane over one of the chromium catalysts, found that, under the selected conditions, the reaction of catalytic dehydrogenation of tetraethylsilane did not take place (^1). Continuing work in this direction, we succeeded in selecting a catalyst* and determining the conditions for the dehydrogenation process of one of the mixed tetraalkylsilanes—trimethylbutylsilane.

Experiments carried out at the same space velocity (30) showed that at temperatures of 550–575° yields of trimethylbutenylsilane of 6.2–8.6% are achieved, calculated on the trimethylbutylsilane passed through (Table 1). The catalyst is distinguished by high stability: during continuous operation for 20 hours the yields of the silicon olefin remain unchanged, and no deposition of silicon on the catalyst is observed. The indicated yields of trimethylbutenylsilane can be substantially increased by repeated passes of the condensates over the catalyst, since the condensates contain considerable amounts of unchanged trimethylbutylsilane.

Table 1

Temperature, °C	Condensate yield, % of the silicon hydrocarbon passed through	Iodine numbers of condensates	Content of trimethylbutenylsilane in condensates, %	Trimethylbutenylsilane yield, % of the silicon hydrocarbon passed through	Hydrogen yield, % of the silicon hydrocarbon passed through	Propylene yield, % of the silicon hydrocarbon passed through
475	77.6	9.7	4.9	3.6	1.8	2.0
500	84.0	7.3	3.7	3.1	1.1	1.7
525	78.7	7.8	3.9	3.1	1.3	4.2
550	69.4	17.7	9.0	6.2	1.6	3.6
575	41.3	41.4	20.8	8.6	6.2	16.3
600	22.0	49.8	25.4	5.6	7.2	18.0

Along with the dehydrogenation reaction, especially at high temperatures (575–600°), certain side reactions occur that are associated with the thermal decomposition of trimethylbutylsilane. Of particular interest is the reaction forming tetramethylsilane and propylene, which proceeds with cleavage of the C—C bond in the butyl radical. At these same temperatures, destructive hydrogenation of the tetramethylsilane at the expense of hydrogen obtained during the dehydrogenation of trimethylbutylsilane. The indicated transformations may be represented by the following scheme:

$$
\begin{gathered}
(CH_3)_3SiCH_2CH_2CH_2CH_3 \xrightarrow[550-575^\circ]{-2H} (CH_3)_3SiC_4H_7 \\
\downarrow\ 575^\circ{-}600^\circ \\
(CH_3)_4Si + CH_2{=}CH{-}CH_3 \\
\downarrow\ +2H \\
(CH_3)_3SiH + CH_4
\end{gathered}
$$

The content of the silicon olefin in the condensates was calculated from the rhodanine numbers, determined by the method of A. A. Bugorkova, L. N. Petrova, and V. M. Rodionov (^{2}). Rhodanination was carried out after five minutes' boiling of the condensates in order to remove $(CH_3)_3SiH$, the product of the side reaction.

The following isomers of trimethylbutenylsilane are theoretically possible: $(CH_3)_3SiCH{=}CHCH_2CH_3$ (cis and trans forms) (I), $(CH_3)_3SiCH_2CH{=}CHCH_3$ (cis and trans forms) (II), $(CH_3)_3SiCH_2CH_2CH{=}CH_2$ (III). However, only

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trimethyl-γ-butenylsilane (III) is known. We were probably unable to isolate the silicon olefin in pure form, since all isomers of trimethylbutenylsilane should have boiling points close both to one another and to that of the initial trimethylbutylsilane. On repeated distillation of the condensates, fractions of 109-111°, 111-114°, and 115-116° were obtained. The constants of the 109-111° fraction, most enriched in silicon olefin, are compared in Table 2 with the properties of the known γ-isomer (III) and of the initial trimethylbutylsilane.

Table 2

Silicon hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}
$(CH_3)_3SiCH_2CH_2CH{=}CH_2$ (^{3})	111.5-112 (750 mm)	0.7358	1.4148
Fraction 109-111°	102-111	0.7375	1.4117
$(CH_3)_3SiCH_2CH_2CH_2CH_3$ (^{4})	115	0.7181	1.4030

The silicon olefin obtained by us is apparently trimethyl-α-butenylsilane (I). Thus, in the Raman spectrum of the 109-111° fraction, combined with the intermediate 111-114° fraction, in addition to the frequencies characteristic of trimethylbutylsilane, frequencies in the region of multiple bonds were also found: 1588, 1607, and 1628 cm^{-1}. The fact that the frequency of the double bond increases from 1594 cm^{-1} in vinylsilanes to 1623 cm^{-1} in isocrotylsilanes is known from the work of A. D. Petrov and co-workers (^{5}). Consequently, displacement of the multiple bond to the second position from the end of the chain causes an increase of its characteristic frequency by 30 cm^{-1}, as is usually observed also in alkenes. It is further known that in isocrotylsilanes a set of stable frequencies is observed: 1064, 1310, 1370, and 1623 cm^{-1}. In our spectrum there are lines at 1056, 1309, 1373, and 1628 cm^{-1}. The formation of trimethyl-β-butenylsilane (II) and trimethyl-γ-butenylsilane (III) is spectrally refuted by the absence of the characteristic frequencies for β- and γ-alkenylsilanes (1640-1655 cm^{-1}) and of the frequency 3080 cm^{-1}, characteristic of a compound with a terminal $= CH_2$ group. Thus, optical analysis indicates the presence in the reaction products of trimethyl-α-butenylsilane, possibly in the form of a mixture of cis and trans isomers.

The absence of the β-isomer (II) is also confirmed by study of the rhodanination rate of the silicon olefin obtained. It is known that β-alkenylsilanes

add rhodan almost quantitatively in 5 min, whereas α- and γ-alkenylsilanes react completely with rhodan only after 24 h (5). In our case, addition of rhodan in 5 min occurred only to 5%, in 1 h to 7.5%, and completely within 24 h.

Finally, the absence of the β-isomer is indicated by the fact that a stable dibromide of trimethylbutenylsilane was obtained. The dibromide was prepared from condensates from experiments at 575° by slow addition of a 0.5 N solution of bromine in chloroform with stirring and external cooling with ice. The dibromide had b.p. 88-90°/8 mm, d_4^{20} 1.3581 and n_D^{20} 1.4918.

Found %: Br 55.68; 55.79
$C_7H_{16}Br_2Si$. Calculated %: Br 55.52

It should be assumed that, if the β-isomer were present, the bromination products should have contained $(CH_3)_3SiBr$—the product of β-cleavage:

$$(CH_3)_3SiCH_2CH = CHCH_3 \xrightarrow{+Br_2} (CH_3)_3SiCH_2CHBrCHBrCH_3 \rightarrow$$
$$\rightarrow (CH_3)_3SiBr + CH_2 = CHCHBrCH_3 \xrightarrow{+Br_2} CH_2BrCHBrCHBrCH_3.$$

Tetramethylsilane was isolated in pure form upon distillation of the condensates as a 26-27° fraction, having d_4^{20} 0.6428 and n_D^{20} 1.3601 (according to (6), b.p. 26.5°, d_4^{20} 0.646, n_D^{20} 1.3591).

Propylene, present in the gas from the experiments, was converted by bromination into the dibromide with b.p. 141-142°, d_4^{20} 1.9322 and n_D^{20} 1.5200; according to (7), b.p. 141.6°, d_4^{20} 1.933, n_D^{20} 1.5203).

Found %: Br 78.84; 78.94
$C_3H_6Br_2$. Calculated %: Br 79.17

Trimethylsilane (b.p. 9°), present in the gas from the experiments, upon bromination of the gas was converted into $(CH_3)_3SiBr$, as evidenced by the presence of an 82-84° fraction obtained during fractionation of the bromination products. After treatment of this fraction in an ethereal solution with 1N NaOH and subsequent purification, a 98-99° fraction (n_D^{20} 1.3860) was obtained, which was $(CH_3)_3SiOH$ (according to (8), b.p. 100°, n_D^{20} 1.3880).

Methane was determined by combustion at 900° on a gas analyzer of the VTI system.

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REFERENCES

1. B. N. Dolgov, G. V. Golodnikov, N. E. Glushkova, ZhOKh, **26**, 1688 (1956).

2. A. A. Bugorkova, L. N. Petrova, V. M. Rodionov, ZhOKh, **23**, 1811 (1953).
3. A. D. Petrov, G. I. Nikishin, Izv. AN SSSR, OKhN, 1952, 1128.
4. F. S. Whitmore, L. H. Sommer et al., J. Am. Chem. Soc., **68**, 475 (1946).
5. A. D. Petrov, Yu. P. Egorov et al., Izv. AN SSSR, OKhN, 1956, 50.
6. G. Aston, R. Kennedy, J. Am. Chem. Soc., **62**, 2567 (1940).
7. *Chemist' s Handbook*, ed. by B. P. Nikol' skii, B. N. Dolgov et al., **2**, 1951.
8. R. O. Sauer, J. Am. Chem. Soc., **66**, 1707 (1944).

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