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REACTION OF ORGANOSILICON COMPOUNDS ON METALS

I. EXCHANGE OF SILYL HYDROGEN WITH DEUTERIUM GAS ON COPPER

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Summary

It is demonstrated in the cases of triethylsilane and *Z*- and *E*-1,2-dimethylsilacyclopentanes that Cu is an active catalyst of the exchange occurring on the action of D_2, accompanied by retention of configuration. This is the first report of the copper-catalysed exchange of H atoms bonded to silicon.

Introduction

Study of H—D exchange has provided essential information on the mechanisms of reactions between metals and hydrocarbons [1]. Although very important results have been reported concerning the reactions of organosilicon compounds on metals, including the Si—H + D_2 reaction [2—6], very little information is available as yet on the metal-catalysed transformations of compounds containing Si—C and Si—H bonds.

Since we could find no published experimental observations on the transformations of organosilicon compounds on Cu, as our first task we set out to study the Si—H + D_2 exchange on Cu. The choice of Cu as catalyst was based on the following reasons, among others:

(a) as a typical *s* metal, its comparison with the *d* metals as regards activity in the exchange reaction;
(b) it has been demonstrated experimentally [7] that D_2 is chemisorbed dissociatively on Cu above 50°C;
(c) on Cu below 400°C, the C—H + D_2 reaction is practically not observed [8] (on this basis a high selectivity is to be expected in the case of compounds containing Si—H bonds);
(d) another *s* metal, Au, has proved an extremely active catalyst for the exchange of H atoms bonded to silicon [4].

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Results and discussion

Some typical experimental data are listed in Table 1. The results clearly show the following:

(1) Since no reaction can be observed at all on the support alone, while the exchange reaction is selective on Cu, the exchange observed on the supported Cu catalyst is evidently to be ascribed to the catalytic role of the copper.

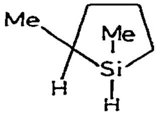
(2) In contrast with the alkanes (no exchange was observed in the case of 4) the silanes are chemisorbed on copper.

(3) The Si—H + D_2 → Si—D + HD exchange proceeds with 100% selectivity.

(4) Since the isomerizations 2 $\rightleftharpoons$ 3 did not occur in the course of the exchange, the reaction Si—H → Si—D was accompanied by retention of the configuration of the silicon atom.

Et_3SiH

1



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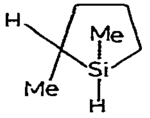

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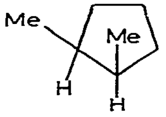


4

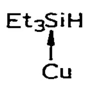
The experimental results show that, as a consequence of the interaction between the occupied *d* orbitals of the Cu and the empty *d* orbitals of the Si, the silanes are adsorbed on Cu via the Si atom. Thus, the exchange may take place via associative surface species of types 1A, 2A and 3A, and dissociative surfaces species of types 1B, 2B and 3B, as for other metals [4—6].

For the interpretation of our experimental results, we propose the reaction mechanism outlined in Scheme 1 (naturally, the reaction schemes are analogous for the exchanges of 2 and 3). Our experimental results reveal that the appropriately pretreated Cu catalyst is suitable for the selective deuteration of organosilicon compounds without the application of extreme conditions. Suitable refinement of the experimental technique may permit research into the mechanism of the catalysis on Cu, by means of investigations of previously unknown reactions on Cu.

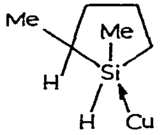
TABLE 1

THE EXCHANGE OF 1, 2, 3 AND 4 WITH MOLECULAR DEUTERIUM

Compound	Catalyst	Temp. (°C)	Conversion (%)	Si—D Selectivity (mol%)
1	Cab-O-Sil	200	0	0
1	Cu	250	95 ± 5	100
1	5% Cu on Cab-O-Sil	30	0	0
1		100	85 ± 5	100
1		150	90 ± 5	100
2		150	90 ± 5	100
3		150	90 ± 5	100
4		400	0	0



1A



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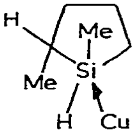
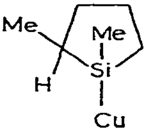


3A

1B



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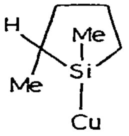
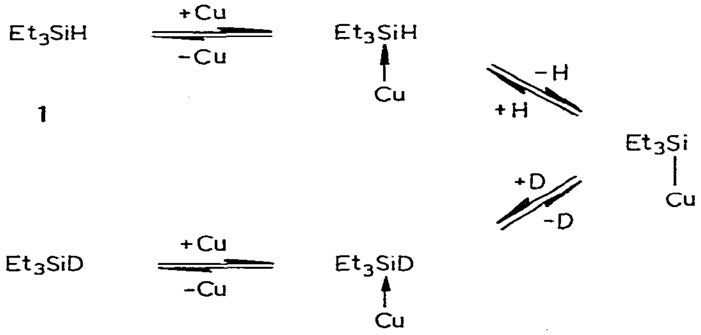


3B

SCHEME 1



Experimental

Materials

Triethylsilane (1) was a commercially available product of Fluka. *Z*- and *E*-1,2-dimethylsilacyclopentane (2 and 3) were prepared on the basis of the literature [9]. The isomers were separated on a Fischer concentric tube column at normal pressure; bp. of 2: 116°C, bp. of 3: 113°C. 1,2-Dimethylcyclopentane (4) was synthesized by using the method in the literature [10]. Deuterium gas was prepared from D_2O with a General Electric 15EHG2B4 generator.

Catalysts

Cu was prepared from CuO by reduction in a deuterium stream of 20 ml min^{-1} at 200, 250 and 300°C, for 1 h at each temperature. Activation of 5% Cu on Cab-O-Sil catalyst [11] was performed in the same way. With a view to homogenation of their activities, the catalysts were pretreated, after activation, by passing the appropriate reactant through them for 2 hours at 200°C, the experimental conditions otherwise being the same as those used for measurement. Such pretreated catalysts retained their activities for a relatively long time (~10 hours).

Method

Measurements were made in the vapour phase in a flow microreactor with 50 mg Cu or 25 mg 5% Cu on Cab-O-Sil catalysts. A Sinter-glass vapour saturator was used for addition of substances. Reactants were passed through the catalysts in deuterium gas (feeding rates: 50—80 mg reactant h^{-1}; 5—6 ml D_2 min^{-1}; D_2: reactant mole ratio ~30). The compounds formed were identified, after isolation, on the basis of their GLC retention times. Determination of Si—D and of C—D concentration was carried out by quantitative evaluation of the characteristic IR [4], ^{1}H NMR and ^{13}C NMR absorption bands, with the aid of calibration curves.

Acknowledgements

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References

1 C. Kemball, Adv. Catal., 11 (1959) 223; J.L. Garnett and W.A. Sollich-Baumgartner, Adv. Catal., 16 (1966) 95; R.L. Burwell, Catal. Rev., 7 (1973) 25.

2 V.A. Ponomarenko, G.V. Odabashyan and A.D. Petrov, Dokl. Akad. Nauk SSSR, 131 (1960) 321.

3 L.H. Sommer, J.E. Lyons, H. Fujimoto and K.W. Michael, J. Amer. Chem. Soc., 89 (1967) 5483; L.H. Sommer, J.E. Lyons and H. Fujimoto, J. Amer. Chem. Soc., 91 (1969) 7051; M.W. Roberts and J.R.H. Ross, J. Chem. Soc., Faraday I, 68 (1972) 221.

4 D.I. Bradshaw, R.B. Moyes and P.B. Wells, J. Chem. Soc., Chem. Commun., (1975) 137; D.I. Bradshaw, R.B. Moyes and P.B. Wells, Sixth Int. Congr. Catalysis, 2 (1976) 1042.

5 D.I. Bradshaw, R.B. Moyes and P.B. Wells, J. Chem. Soc., Faraday I, 76 (1980) 979.

6 M.A. Long, J.L. Garnett, C.A. Lukey and P.G. Williams, Aust. J. Chem., 33 (1980) 1393.

7 R.J. Mikovsky, M. Boudart and H.S. Taylor, J. Amer. Chem. Soc., 76 (1954) 3814; M. Kiyomiya, N. Momma and I. Yasumori, Bull. Chem. Soc. Japan, 47 (1974) 1852.

8 A. Frennet, Catal., Rev., 10 (1975) 37; A. Ozaki, Isotopic Studies of Heterogeneous Catalysis, Kodansha-Acad. Press, Tokyo-New York-London, 1977.

9 F.K. Cartledge, J.M. Wolcott, J. Dubac, P. Mazerolles and M. Joly, J. Organometal. Chem. 154 (1978) 187.

10 A.L. Liberman, O.V. Bragin, G.K. Gur'yanova and B.A. Kazanskii, Dokl. Akad. Nauk SSSR, 148 (1963) 591.

11 M. Bartók and Á. Molnár, J. Chem. Soc., Chem. Commun., (1980) 1178.