

Direct synthesis of organochlorosilanes by the reaction of metallic silicon with hydrogen chloride and alkene/alkyne

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Organosilicon compounds were directly synthesized from metallic silicon, alkene/alkyne and HCl, EtHSiCl₂ being obtained with 47% selectivity from Si, C₂H₄ and HCl at 513 K, and CH₂=CHSiHCl₂ and EtHSiCl₂ with 39 and 23% selectivity, respectively, when C₂H₂ was used in place of C₂H₄.

Methylchlorosilanes, especially dimethyldichlorosilane, are produced industrially by the reaction of metallic silicon with MeCl using a copper catalyst.¹ The direct synthesis of dimethyldichlorosilane is the key step for synthesizing silicone polymers. Various mechanisms have been proposed for this direct synthesis.² We carried out the reaction in the presence of butadiene as a silylene trapping agent and found that an appreciable amount of silacyclopent-3-enes was formed together with methylchlorosilanes.³ This indicates the intermediacy of silylene-type species in this heterogeneous reaction. It was presumed that the silylene species are formed on the surface of a silicon–copper alloy, through which silicon atoms diffuse out to the surface from the phase of metallic silicon. The intermediacy of the silylene species has also been proposed for the selective formation of trialkoxysilanes in the direct reactions of metallic silicon with alcohols.⁴

HCl also reacts with metallic silicon to afford chlorosilanes, mainly trichlorosilane.⁵ We presume that the surface silylene is also an intermediate for the selective formation of trichlorosilane.

It is well known that the addition of silylenes to alkenes gives vinylsilanes *via* silacyclopropane intermediates.^{6,7} It is very plausible that silylene species at the surface also react with alkenes to form silacyclopropanes. In previous work, we have reported that ethylmethoxysilanes are obtained by the reaction of metallic silicon, MeOH and C₂H₄.⁸ When allyl propyl ether was used instead of C₂H₄, allyldimethoxysilane was obtained in 38% selectivity.⁹

In this work, we report that alkylsilanes are directly prepared by the reaction of metallic silicon and HCl in the presence of C₂H₄ or propene. Organosilanes are also obtained by the reaction of metallic silicon, HCl and C₂H₂.

The reactions were carried out in a fixed-bed flow reactor. The mixture of metallic silicon (8.9 mmol) and copper(I) chloride (0.79 mmol) as a catalyst was placed in a quartz tube reactor (id 10 mm) and preheated at 723 K for 10 min. Then, HCl (3 mmol h⁻¹) and C₂H₄ (12 mmol h⁻¹) was fed to the reactor at 513 K. The reactor effluents were analyzed every 10 min by GC.

Fig. 1 shows the time courses of the rates of formation of products and cumulative conversion of silicon. Ethyldichlorosilane and trichlorosilane were obtained as the main products. The rates of formation of these products increased to the maximum with reaction time and then decreased. Small amounts of dichlorosilane and tetrachlorosilane were also formed. The cumulative conversion of silicon reached 36% in 12 h. Though the reaction was stopped at 12 h in the experiment in Fig. 1, further increases in silicon conversion would be attained on further extending reaction time. The overall selectivity for ethyldichlorosilane for 12 h was 47%. The

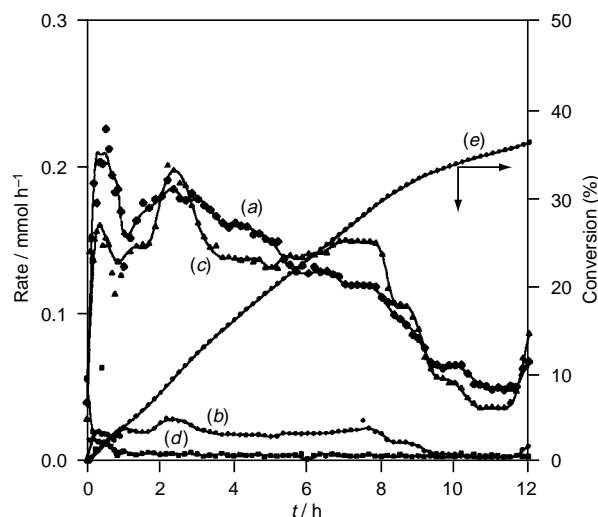


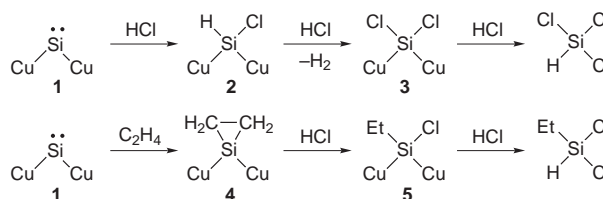
Fig. 1 Time courses of formation rates of the products and cumulative conversion of silicon in the reaction of silicon, HCl and C₂H₄. Preheating: 723 K for 10 min; reaction: 513 K, Si: 8.9 mmol, CuCl: 0.79 mmol. Feed: HCl (3 mmol h⁻¹) and C₂H₄ (12 mmol h⁻¹). Rates of formation of (a) ethyldichlorosilane, (b) dichlorosilane, (c) trichlorosilane, (d) tetrachlorosilane and (e) conversion of silicon.

selectivities for dichlorosilane, trichlorosilane and tetrachlorosilane were 6, 45 and 2%, respectively.

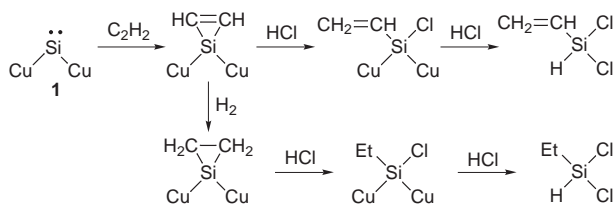
Note that ethyldichlorosilane was the sole organosilane produced. To explain this fact, we propose the following reaction scheme involving surface silylene **1** as shown in Scheme 1. In the absence of C₂H₄, the surface silylene reacts with HCl. The subsequent reactions through surface species **2** and **3** lead to the formation of HSiCl₃ as the main product. The formation of HSiCl₃ by the addition of HCl to dichlorosilylene has been reported.¹⁰ The silylene intermediate **1** reacts with C₂H₄ to form silacyclopropane species **4**. The species **4** is converted into the surface species **5** by attack of HCl. Finally attack of HCl on the species **5** leads to the cleavage of the two Si–Cu bonds to form ethyldichlorosilane.

Use of propene instead of C₂H₄ under similar conditions resulted in the formation of propyldichlorosilane and isopropyldichlorosilane with the selectivities of 10 and 24%, respectively, together with chlorosilanes.

When C₂H₂ was used instead of alkenes, vinylchlorosilane and ethyldichlorosilane were produced. After preheating the



Scheme 1



Scheme 2

Table 1 Effect of $C_2H_2 : HCl$ ratio on the $Si-HCl-C_2H_2$ reaction^a

$C_2H_2 : HCl$ ratio	Si conversion (%)	$(C_2H_3)-HSiCl_2$ (%)	$EtHSiCl_2$ (%)	H_2SiCl_2 (%)	$HSiCl_3$ (%)	$SiCl_4$ (%)
0.33	15	27	15	4	53	1
0.26	16	34	21	0	45	0
0.2	31	23	11	4	61	1
0.13	37	22	11	5	62	1
0.07	67	10	3	11	76	1
0	85	—	—	6	93	1

^a Preheating: 723 K for 10 min; reaction: 513 K for 5 h, Si: 8.9 mmol, Cu: 0.20 mmol, HCl: 15 mmol h^{-1} .

silicon–CuCl mixture at 723 K, only HCl (15 mmol h^{-1}) was fed at 513 K for 10 min. During this period, 1% of silicon charged in the reactor was consumed to form chlorosilanes, the main product being $HSiCl_3$. Then, the feed of HCl was changed to a mixture of HCl (15 mmol h^{-1}) and C_2H_2 (4 mmol h^{-1}). Vinyl-dichlorosilane and ethyl-dichlorosilane were produced together with chlorosilanes. The overall selectivities in the 5 h reaction for vinyl-dichlorosilane and ethyl-dichlorosilane were 39 and 23%, respectively, these two organosilanes accounting for 62% of the products. About 13% of silicon charged in the reactor was consumed in 5 h. A plausible mechanism for the formation of vinyl- and ethyl-dichlorosilane is shown in Scheme 2.

The silylene intermediate **1** reacts with C_2H_2 to form a silacyclopropene surface species, which is attacked by HCl to form a surface species containing a vinyl group. Silacyclopropene intermediates are often postulated in the reaction of silylenes with alkynes, though normally only dimeric products, 1,4-disilacyclohexa-2,5-dienes are obtained.^{7,11} The exclusive formation of monomeric products indicates the silylene species do not exist in the vapor phase, but are located on the surface. Formation of ethyl-dichlorosilane indicates that the hydrogenation of the intermediate(s) occurs on the surface.

Table 1 shows the effect of the $C_2H_2 : HCl$ molar ratio on the product distribution. Without C_2H_2 , high conversion of metallic silicon is attained, giving trichlorosilane as a main product. As

the $C_2H_2 : HCl$ ratio increases, the reactivity of metallic silicon decreases. The selectivity for organosilanes was highest at a $C_2H_2 : HCl$ ratio of 0.26.

The reactions of silicon, HCl and alkene/alkyne offer a new method for synthesizing organosilanes directly from metallic silicon.

Notes and References

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- R. J. H. Voorhoeve, *Organohalosilanes: Precursors to Silicones*, Elsevier, Amsterdam, 1967.
- D. H. Hurd and E. G. Rochow, *J. Am. Chem. Soc.*, 1945, **67**, 1057; A. L. Klebansky and V. S. Fikhtengolts, *J. Gen. Chem. USSR*, 1956, **26**, 2795; R. J. H. Voorhoeve and J. C. Vlugter, *J. Catal.*, 1965, **4**, 220; I. M. Podgorny, S. A. Golubtsov, K. A. Andrianov and E. G. Mangalin, *J. Gen. Chem. USSR*, 1974, **44**, 739; M. P. Clarke, *J. Organomet. Chem.*, 1989, **376**, 165, and references therein; K. M. Lewis, D. McLeod, B. Kanner, J. L. Falconer and T. Frank, in *Catalyzed Direct Reactions of Silicon*, ed. K. M. Lewis and D. G. Rethwisch, Elsevier, Amsterdam, 1993, pp. 333–440, and references therein.
- M. Okamoto, S. Onodera, T. Okano, E. Suzuki and Y. Ono, *J. Organomet. Chem.*, 1997, **531**, 67.
- M. Okamoto, E. Suzuki and Y. Ono, *J. Catal.*, 1994, **145**, 537; M. Okamoto, K. Yamamoto, E. Suzuki and Y. Ono, *J. Catal.*, 1994, **147**, 15.
- I. Shihara and J. Iyoda, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 636; B. Kanner and K. M. Lewis, in *Catalyzed Direct Reactions of Silicon*, ed. K. M. Lewis and D. G. Rethwisch, Elsevier, Amsterdam, 1993, pp. 1–66, and references therein; W. C. Breneman, in *Catalyzed Direct Reactions of Silicon*, ed. K. M. Lewis and D. G. Rethwisch, Elsevier, Amsterdam, 1993, pp. 441–457.
- P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, 1964, **86**, 1442; V. J. Tortorelli, M. Jones, Jr., S. Wu and Z. Li, *Organometallics*, 1983, **2**, 759; M. Ishikawa, K. Nakagawa and M. Kumada, *J. Organomet. Chem.*, 1979, **178**, 105.
- P. P. Gaspar, in *Reactive Intermediates*, ed. M. Jones, Jr., and R. A. Moss, Wiley, New York, 1981, vol. 2, pp. 335–385, and references therein; Y.-N. Tang, in *Reactive Intermediates*, ed. R. A. Abramovitch, Plenum Press, New York, 1982, vol. 2, pp. 297–366, and references therein.
- M. Okamoto, N. Watanabe, E. Suzuki and Y. Ono, *J. Organomet. Chem.*, 1995, **489**, C12.
- M. Okamoto, E. Suzuki and Y. Ono, *J. Chem. Soc., Chem. Commun.*, 1994, 507.
- R. C. Bracken, U.S. Patent 3 565 590, 1971.
- T. J. Barton, J. A. Kilgour, *J. Am. Chem. Soc.*, 1974, **96**, 7150; E. A. Chernyshev, N. G. Komalenkova, S. A. Bashkurova and V. V. Sokolov, *Zh. Obshch. Khim.*, 1978, **48**, 830; E. A. Chernyshev, N. G. Komalenkova and S. A. Bashkurova, *Zh. Obshch. Khim.*, 1971, **41**, 1175; M. Ishikawa, K. Nakagawa and M. Kumada, *J. Organomet. Chem.*, 1977, **131**, C15; W. H. Atwell, D. R. Weyenberg, *J. Am. Chem. Soc.*, 1968, **90**, 3438.

Received in Cambridge, UK, 5th January 1998; 8/001211