

Metal-Catalysed Exchange of Alkyl and Silyl Hydrogen in Organosilanes with Tritium Gas over Raney Nickel as Measured by ^3H N.M.R.

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Abstract

Analysis by tritium n.m.r. of triethylsilane, tetramethylsilane, hexamethyldisiloxane and chlorodimethylsilane exchanged with tritium gas over Raney nickel at 100°C shows that exchange readily occurs in alkyl substituents as well as with silyl hydrogen; novel species involving charge-transfer intermediates in dissociative adsorption at the C-H as well as the Si-H bonds are proposed to explain the data.

We report for the first time that alkyl hydrogen exchange accompanies silyl hydrogen exchange when organosilanes are exposed to tritium gas over Raney nickel and demonstrate the relative rates of primary and secondary hydrogen exchange in the alkyl substituent of triethylsilane. Recently it was noted¹ that siloxanes could be tritiated to high specific activity by a similar exchange reaction. It thus appears that alkyl exchange is a general feature of the silanes, including partially alkylated molecules, as well as siloxanes.

Previous studies of exchange of partially alkylated silanes with deuterium gas over a variety of metal surfaces have noted that exchange was confined to the silyl hydrogen.²⁻⁴ Mass spectrometric analysis, though complicated by fragmentation of the parent ion,⁵ demonstrated the absence of exchange of hydrogen of the alkyl substituents² and the results were interpreted as indicating the strong preferential association of the molecule with the metal surface by adsorption at the silicon atom. It is thus of considerable significance in terms of surface catalytic mechanisms that our ^3H n.m.r. study of the exchange of a molecule such as triethylsilane demonstrates that experimental conditions may be chosen where exchange occurs with the hydrogen of the alkyl substituent as well as the silyl hydrogen over Raney nickel.

Exchange of alkylsilanes, haloalkylsilanes and siloxanes with tritium gas all exhibit isotope incorporation within alkyl substituents (Table 1). The ^3H n.m.r. spectrum of triethylsilane (Fig. 1) obtained with broadband proton decoupling, as

¹ Long, M. A., Garnett, J. L., and Lukey, C. A., *Org. Magn. Reson.*, 1979, **12**, 551.

² Bradshaw, D. I., Moyes, R. B., and Wells, P. B., *J. Chem. Soc., Chem. Commun.*, 1975, 137.

³ Bradshaw, D. I., Moyes, R. B., and Wells, P. B., *Proc. 6th Int. Congr. Catalysis, London*, 1976, **2**, 1042.

⁴ Sommer, L. H., Lyons, J. E., and Fujimoto, H., *J. Am. Chem. Soc.*, 1969, **91**, 7051.

⁵ Bradshaw, D. I., Moyes, R. B., and Wells, P. B., *Can. J. Chem.*, 1976, **54**, 599.

described elsewhere,^{6,7} demonstrates the power of the ^3H n.m.r. technique in showing unequivocally the orientation of exchange within the molecule. Hydrogens of the methyl as well as the methylene position exhibit substantial exchange. In these preliminary experiments the apparent differences in rates between the compounds listed may not necessarily indicate reactivity trends. Furthermore, chlorodimethylsilane and to a slight extent tetramethylsilane formed a number of unidentified tritiated byproducts as shown by radio-gas chromatography analysis.

Table 1. Tritium orientation in silanes

Reaction conditions: Raney nickel (0.1 g), silane (0.2 ml) and tritium gas (1 Ci) heated to 100°C for specified times. Raney nickel was prepared and degassed as described elsewhere¹

Compound	Reaction time (h)	Activity (mCi/ml)	Incorporated tritium (%)		
			SiH	CH_2	CH_3
Et_3SiH	64	1700	37	38	25
Me_4Si	72	200	—	—	100
$(\text{Me}_3\text{Si})_2\text{O}$	77	1000	—	—	100
Me_2SiHCl	160	800	57	—	43 ^A

^A Tritium distribution is sum of that of the parent and byproduct molecules.

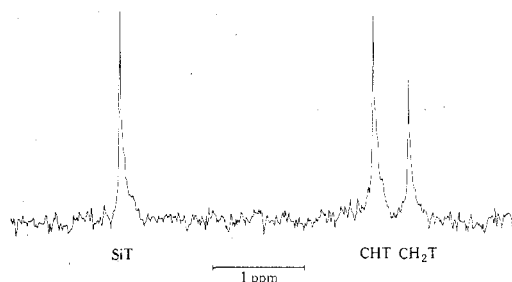
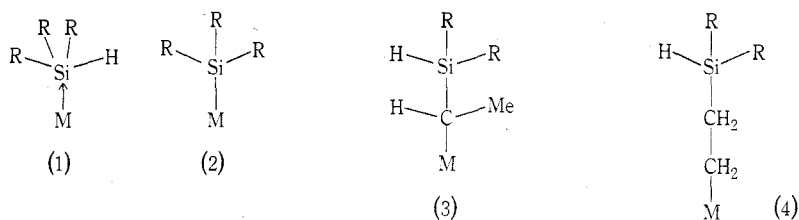


Fig. 1. ^3H n.m.r. spectrum of triethylsilane with broadband proton decoupling.



A significant aspect of the current series of experiments is that to the present time no exchange has been observed between tetramethylsilane and isotopic water (D_2O and HTO) in the presence of Raney nickel, activated platinum, palladium, gold or Raney cobalt at temperatures up to 130°C. Furthermore, sodium-borohydride-reduced platinum oxide appeared to be inactive in inducing exchange between hexamethyldisiloxane and tritium gas at 100°C.

⁶ Long, M. A., and Lukey, C. A., *Org. Magn. Reson.*, 1979, **12**, 440.

⁷ Elvidge, J. A., Jones, J. R., Chambers, V. M. A., and Evans, E. A., 'Isotopes in Organic Chemistry' Vol. 4, Ch. 1, and references therein (Elsevier: Amsterdam 1978).

Previous observations of exchange of silyl hydrogen with deuterium gas have led to the postulation that species such as (1) and (2) may exist on a metal surface,² the ability of silicon to exceed four-coordination being well known. The current observation of the formation of silyl hydrogen labelled silanes together with the formation of some byproducts from tetramethylsilane is further evidence for species of type (2). However, it now appears certain that dissociative σ -bonded species such as (3) and (4) also form on the surface of Raney nickel. These species are analogous to those participating in the generally accepted exchange mechanisms of alkanes on metal surfaces. Interconversion of species (3) and (4) through π -olefin type intermediates is feasible. The present results also raise the interesting possibility that primary adsorption of the molecule may occur through the alkyl hydrogens followed by interconversions (π -complexed intermediates) between (2) and (3), leading to exchange in the silyl position. These, and related aspects of the mechanism, are being investigated by deuterium and tritium studies at present.

In addition to the significance of these results to the understanding of metal catalysis the technique described represents a unique method for the tritiation of silanes to high specific activity for purposes such as ^3H n.m.r. referencing and other tracer studies.

Acknowledgments

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