Ruthenium Metal-catalysed Deuterium Exchange between Organosilanes and Perdeuteriobenzene

By John L. Garnett,* Mervyn A. Long,* and Patra Sriwattanatamma
(*School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033, Australia*)

Summary Ruthenium metal prepared by $NaBH_4$-reduction of RuO_2 possesses unique activity in consistently catalysing hydrogen isotope exchange between organosilanes and C_6D_6, exchange occurring readily in alkyl and aryl positions, particularly in trisubstituted silanes; a modification of the technique can also be used for the tritium labelling of these silanes.

We recently reported the application of Raney nickel for labelling silanes by exchange with tritium gas for n.m.r. reference purposes.[1] However, following extensive tests of a variety of bulk and supported metals for consistent catalytic activity towards alkyl and aryl hydrogen isotope exchange in organosilanes, we now report that ruthenium metal appears to exhibit unique reactivity for the labelling of these compounds when compared with other transition and noble metals such as platinum, palladium, rhodium, iridium, and nickel. C_6D_6 is used as isotope source and the work constitutes the first reported study of deuteriation of a variety of organosilanes by exchange in which elemental gas is not involved.

A recent study[2] of methylsilane reactions over nickel, rhodium, and tungsten films at 195 K led the authors to conclude that both exchange with D_2 and mutual exchange between silane molecules was confined to the silyl group, no deuterium incorporation being observed in the alkyl substituent. The results were similar to those reported for gold and molybdenum films in an earlier study.[3] It was proposed[2] that the silicon–metal bond of the adsorbed species becomes stronger as alkyl substituents on the silicon are replaced with hydrogen in the reactant molecule, and that when silicon has fewer than two substituents, the formation of the adsorbed species by dissociation of the hydrogen attached to the silicon was not reversible, so producing some poisoning of the catalyst.

It is thus significant that the results in the Table show that ruthenium catalyses exchange of both alkyl and aryl substituents of silanes with the isotope source C_6D_6, except where the silicon bears four alkyl or phenyl substituents. Four benzyl substituents do not preclude exchange. Furthermore, exchange appears to be most facile when *three* alkyl or aryl substituents are attached to silicon. Thus,

Table. Deuteriation of silanes by exchange with C_6D_6 over ruthenium metal.[a]

Compound	D_{eq}[b] (%)	D_{obs} (%)	Deuterium distribution[c]							
			D_0	D_1	D_2	D_3	D_4	D_5	D_6	ΣD_{7+}
Et_2SiH_2	47	1·4	86	12·5	1·6	0·2				
Et_3SiH	51	14	9·4	49	18	8·3	4·4	2·6	2·3	6·4
Et_4Si	51	nil								
$Pr^n{}_3SiH$	52	4·2	15·5	78	4·0	2·1	0·4			
Ph_2SiH_2	51	3·4	65·5	28	4·6	0·7	0·2			
Ph_3SiH	50	26·5	1·1	5·0	12·2	19·2	21·4	17·6	12	11·5
Ph_2MeSiH	49	6·1	40	40	14·5	4·3	0·9			
$PhMe_2SiH$	46	20·5	7·6	21·2	26·7	21·7	12·9	6·2	2·6	1·0
$PhMe_3Si$	45	nil								
$PhCH_2Me_3Si$	44	5·5	42	36	16·0	4·9	1·0			
Et_3SiH[d]	50	0·3	94	5·8	0·1					
Ph_3SiH[e]	50	2·2	70	26	2·3	1·3				

[a] Reaction conditions: Ru (0·01 g) prepared by $NaBH_4$-reduction of RuO_2, silane (0·05—0·10 ml), and C_6D_6 (0·1 ml), heated to 150 °C for 3 days. [b] Equilibrium % of deuterium, calculated on the assumption that all hydrogen in silane is exchangeable. [c] Deuterium distribution from low-voltage mass spectrum of parent ion. [d] 40% mole ratio of Et_2SiH_2 included in reaction mixture. [e] 40% mole ratio of Ph_2SiH_2 included in reaction mixture.

for example, triethylsilane exchanges more readily than diethylsilane, while tetraethylsilane appears to be inert.

Attempts to observe similar exchange reactions over ruthenium when D_2O was used as isotope source instead of C_6D_6 were largely unsuccessful, many of the silanes tending to decompose when heated with water. Reactions of silanes with C_6D_6 over a variety of other metal catalysts occasionally showed some exchange but the pattern was not consistent. Thus, for example, diphenylsilane showed exchange with C_6D_6 over rhodium metal but diethylsilane was inert.

The results demonstrate that by suitable selection of a metal it will be possible to extend our understanding of catalysis by metals from reactions of carbon compounds to their silicon analogues. As has been pointed out previously[2] the ability of silicon to exceed four co-ordination provides for the possibility that silanes may adsorb associatively whereas alkanes are not usually considered to do so. However, at this early stage of the investigation of silane exchange it is not possible to distinguish associative from dissociative mechanisms clearly. For exchange to proceed between C_6D_6 and a silane, both must be activated in turn on the catalytic surface. Neither species may adsorb to the complete exclusion of the other. Thus it may be that the relatively low activity of molecules of type R_2SiH_2 when compared with R_3SiH may be attributable to strongly adsorbed dissociative species of the type $R_2Si{=}*$ ($*$ = surface), as previously proposed.[2] This suggestion is supported by the final two results reported in the Table which show that the addition of the disubstituted analogue, R_2SiH_2, to the reaction mixture substantially poisons the exchange of the trisubstituted silane, R_3SiH.

The observation that pure trisubstituted silanes, R_3SiH, consistently exhibit high reactivity and will exchange readily to equilibrium confirms that adsorbed species of the type $R_3Si{-}*$ do not poison the surface and by analogy with alkane exchange it is likely that interconversion of species of this type with molecules adsorbed at alkyl or aryl positions may readily occur. A brief investigation[1] of the exchange between tritium gas and triethylsilane over Raney nickel in which tritium was shown by ^3H n.m.r. spectroscopy[4] to be distributed between all positions of the molecule led to the proposal that the position of adsorption of the molecule may migrate by $\sigma \rightarrow \pi \rightarrow \sigma$ interconversions between dissociatively adsorbed intermediates as proposed previously for alkanes. Analogous mechanisms appear to operate in the benzene–silane exchange system.

Additional preliminary studies indicate that ruthenium also will be the most efficient metal catalyst for labelling organosilanes to high specific activity for tritium n.m.r. spectroscopy applications.

We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Sciences and Engineering for support.

(*Received, 12th May* 1981; *Com.* 561.)

---

[1] M. A. Long, J. L. Garnett, C. A. Lukey, and P. G. Williams, *Aust. J. Chem.*, 1980, **33**, 1393; M. A. Long, J. L. Garnett, and C. A. Lukey, *Org. Magn. Reson.*, 1979, **12**, 551.

[2] D. I. Bradshaw, R. B. Moyes, and P. B. Wells, *J. Chem. Soc., Faraday Trans.* 1, 1980, **76**, 979.

[3] D. I. Bradshaw, R. B. Moyes, and P. B. Wells, *J. Chem. Soc., Chem. Commun.*, 1975, 137; Proc. Sixth Int. Congr. Catalysis, London, 1976, The Chemical Society, London, 1977, vol. 2, p. 1042.

[4] J. L. Garnett, M. A. Long, and C. A. Lukey, *J. Chem. Soc., Chem. Commun.*, 1979, 634; J. M. A. Al-Rawi, J. A. Elvidge, J. R. Jones, R. B. Mane, and M. Saieed, *J. Chem. Res.*, 1980, (*S*) 298, and references therein.