Journal of Organometallic Chemistry, 69 (1974) 185—192
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE MECHANISM OF THE BASE-CATALYSED ALCOHOLYSIS OF TRIORGANOSILANES

C. EABORN and IAN D. JENKINS
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received August 8th, 1973)

Summary

The isotopic composition of the hydrogen evolved on treatment of a triorganosilane in benzene with sodium methoxide in a MeOH/MeOD mixture has been determined for triethyl- and tribenzyl-silane, and the triarylsilanes $(XC_6H_4)_3SiH$ with X = H, *p*-Me, *p*-OMe, *p*-Cl and *m*-CF_3. The magnitude of the isotope effect thus revealed has been found to increase with increasing reactivity of the silicon hydride. It is concluded (*i*) that there is important proton transfer from the solvent to the separating hydride ion in the rate determining step; (*ii*) that the degree of such transfer increases with the reactivity of the organosilane; (*iii*) that there is a bent arrangement of the Si--H--H system in the transition state; and (*iv*) that the simplest mechanism consistent with all the observations is one in which the rate determining cleavage of the Si—H bond follows the rapid, reversible formation of a pentacoordinate silicon intermediate.

The special behaviour of tris(pentafluorophenyl)silane is briefly discussed.

Introduction

The base-catalysed solvolysis of silicon hydrides has been the subject of several mechanistic studies in the past 26 years. The earlier work is summarized in ref. [1], and later work in ref. [2]. The features (a)—(c) below, appear to be firmly established.

(*a*). In the (highest energy) transition state for hydrolysis or alcoholysis, the incoming hydroxide or methoxide ion is fairly tightly bound to the silicon atom, to place a substantial excess of negative charge on that atom, as revealed by the magnitudes of the ρ factors for $(XC_6H_4)_3SiH$ and $XC_6H_4Me_2SiH$ systems. These vary between +2 and +5. (For primary references, see ref. [3].)

(*b*). The kinetic isotope effect k_{SiH}/k_{SiD} (or k_{SiH}/k_{SiT}) for isotopic substitution in the silicon hydride is very small, always < 1.5, and is insensitive to the nature of the organic groups of the hydride [2,3].

(*c*). The proton transfer from the solvent to the separating hydride ion is concerted with the breaking of the Si—H bond. This is revealed by (*i*) the magnitude of the deuterium (or tritium) *product* isotope effect, which we designate PIE, given by the ratio of the H_2 and HD (or HT) products obtained from reaction in SH/SD (or SH/ST) solvent mixtures (e.g. PIE values [3] of 3—7 for $k/_{SH}/k_{ST}$ in aqueous piperidine or aqueous ethanolic alkali)*, and (*ii*) the overall solvent isotope effects on the *rate*, given by the ratio k_{SH}/k_{SD} of rates in SH and SD, respectively; thus a k_{SH}/k_{SD} (rate) ratio of 1.97 was observed for triphenylsilane in methanol [5]. Interpretation of this rate ratio is complicated by the probable existence of substantial secondary isotope effects, but by far the most important of these, that on the reactivity of methoxide ion, would favour a higher rate in MeOD than in MeOH [2,4], and so there must be a substantial primary solvent isotope effect arising from the proton transfer from oxygen to the separating hydride ion.

In the light of the above observations, the main mechanistic choice lies between the two-step process (1), with step (a) fast and reversible, and the concerted process (2). There is then a secondary choice between a linear or a bent arrangement of the atoms in the Si---H---H--- system**.

$$\left.\begin{array}{ll} \mathrm{MeO^- + R_3SiH \rightleftharpoons [MeOSiR_3H]^-} & \text{(a)} \\ \qquad\qquad\qquad\qquad\text{(I)} & \\ \mathrm{[MeOSiR_3H]^- + MeOH \rightarrow MeOSiR_3 + H_2 + MeO^-} & \text{(b)} \end{array}\right\}\text{(1)}$$

$$\mathrm{MeO^- + R_3SiH + HOMe \rightarrow MeOSiR_3 + H_2 + MeO^-} \qquad (2)$$

Schowen and his colleagues do not attempt to decide firmly between these possibilities in either case, but conclude, primarily on the basis of the various isotope effects and of their failure to detect any catalysis by phenoxide ion, that the transition state fairly closely resembles the 5-coordinate silicon complex (I), with the Si—H and H—OMe bonds very little broken and the H—H bond little formed, and that the separating hydride ion does not receive much assistance from the proton transfer from the solvent [2].

In order to throw further light on the problem, we have studied the variation of the magnitude of the PIE with the structure of the silicon hydride.

Results and discussion

The product isotope effect, PIE, was measured by mass spectrophotometric determination of the composition of the hydrogen evolved***. Initially

---

*Schowen and Bacon consider that such product isotope effects do not in themselves rule out the possibility that a free hydride ion separates, since, they say, "whenever proton transfer occurs, selection between isotopic solvent molecules will be observed in a competition experiment" [4]. We, on the contrary, believe that the possibility is indeed ruled out by the substantial PIE's, since a free hydride ion reacts with the solvent without any appreciable activation barrier, i.e. at or close to the encounter rate [5], so that no significant discrimination between SH and SD molecules can be expected.

**Yet another choice concerns the stereochemistry of the reaction at silicon, which we do not discuss because we have obtained no information relevant to it. The stereochemistry of the reaction in methanol is not yet known [6], but all the possible stereochemistries can be reconciled with the mechanism proposed, especially if pseudorotation is allowed within the intermediate (I).

***The absence of any significant amount of D_2 in the evolved gas indicated that there was no appreciable hydrogen exchange between the solvent and the R_3SiH before cleavage.

TABLE 1

THE MAGNITUDES OF THE PRODUCT ISOTOPE EFFECTS (PIE) FOR THE REACTION AT CA. 21° OF R_3SiH COMPOUNDS WITH 2.0 *M* NaOMe IN 1/1 MeOH/MeOD (5 VOL) IN THE PRESENCE OF BENZENE (4 VOL)

R	PIE[a]	R	PIE
Et	2.30	C_6H_5	3.95
Et	2.14[b]	*p*-ClC_6H_4	4.32
$PhCH_2$	2.55	*m*-$CF_3C_6H_4$	5.03
p-MeC_4H_6	3.00	C_6F_5	3.98[c]
p-$MeOC_6H_4$	3.40		

[a] Estimated uncertainty, based on reproducibility, ± 0.1. [b] Value of HD/D_2 obtained with Et_3SiD as starting hydride, after taking into account the 10% Et_3SiH content. [c] A value of 4.03 was obtained with pyridine (ca. 0.5 *M*) as the base instead of sodium methoxide, and a value of 3.70 with an HCl/HDO/MeOH/MeOD medium.

the hydride was added to a 1/1 MeOH/MeOD mixture containing 2*M* NaOMe, but this gave variable results, presumably because much reaction took place before the hydride had fully dissolved, so that the effective medium in the early stages was possibly the hydride containing relatively little methanol. We found that satisfactorily reproducible results were obtained when a benzene solution of the silicon hydride was mixed with 1.25 volumes of 1/1 MeOH/MeOD containing 2*M* NaOMe, and since we were primarily interested in the variation of the isotope effect with structure we mainly used these conditions throughout; the results are shown in Table 1. As a check on the method, the PIE was measured for Et_3SiD, and found to be close to that obtained with Et_3SiH. For one compound, viz. triphenylsilane, however, we examined the PIE obtained on mixing a solution of the hydride in 1/1 MeOH/MeOD with an equal volume of 2*M* NaOMe in 1/1 MeOH/MeOD, and found it to be reproducible and to have a value, viz. 4.0, not significantly different from that obtained with benzene present.

The main features of the results are as follows:

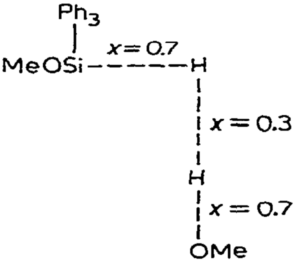
(*i*). The PIEs are quite large. (In so far as comparison can be made, the values are consistent with those observed previously [3] in rather different media.) This confirms that the solvent transfers a proton to the hydride ion as it separates, and there is a significant degree of H—OMe bond breaking in the transition state for the Si—H bond breaking process.

(*ii*). The value of the PIE is sensitive to the change in reactivity of the hydride. In general it increases as the reactivity of the hydride increases for electronic reasons, not only on going from triethyl- to tribenzyl- to triphenylsilane, but also [except for tris(pentafluorophenyl)silane, which is separately discussed below] within the series of substituted triphenylsilanes, $(XC_6H_4)_3$-SiH, as the electron-withdrawing power of X is increased. (There is a minor perturbation in the expected sequence in that the PIE value appears to be slightly smaller for X = *p*-Me than for X = *p*-OMe.) This variation of the solvent PIE with the reactivity of the hydride is in marked contrast to the insensitivity of the k_{SiH}/k_{SiD} rate ratio obtained by labelling of the hydrides [3,4].

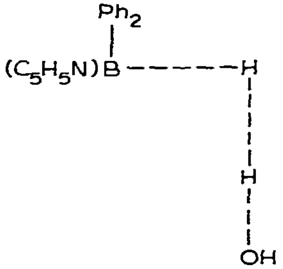
(*iii*). The magnitude of the solvent PIE for triphenylsilane in MeOH/MeOD is consistent with the magnitude of the overall solvent isotope effect, k_{SH}/k_{SD}, viz. 1.97, obtained from the rates of reaction in MeOH and MeOD separately

[2,4]. This is because a secondary isotope effect is expected to favour the attack on silicon by the MeO^- ion in MeOD over that in MeOH by a factor of about 2 [2,7], so that the overall solvent kinetic isotope effect k_{SH}/k_{SD} should be ca. 4.0 × 0.5, i.e. 2.0.

In our view, the two step process represented in eqn. (1), but with a non-linear Si—H—H arrangement in the transition state of the rate-determining step (b), provides conceptually the simplest interpretation of all the results. The bond-orders, x, of the breaking and forming bonds may be as shown in the diagramatic representation (II) of the transition state for triphenylsilane. (For simplicity the incoming proton is shown as attaching directly to the separating hydrogen atom, but in reality it is more likely to attack into the electrons of the Si—H bond [8,9], to give an Si—H—H angle of < 90°.)



(II)



(III)

The advantages of this interpretation are as follows:

(*1*) It is reasonably consistent with the fairly high ρ factor observed for $(XC_6H_4)_3SiH$ and $(XC_6H_4)Me_2SiH$ compounds, since there is a substantial degree of charge (ca. 0.7 of a unit) on the silicon atom. We should note here that it is not necessary for the Si—H bond-breaking and the H—H bond-making to be quantitatively synchronous, and a bond-order of, say 0.5—0.6 for the Si—H bond could be associated with one of 0.3 for the H—H bond in the transition state (II) derived from triphenylsilane, and the 0.5—0.6 of a unit charge which would then lie on the silicon atom in (II) might be more consistent with the observed ρ factors.

(*2*) Because of the non-linear arrangement of atoms in the Si—H—H system in structure (II), it is consistent with the smallness of the k_{SiH}/k_{SiD} ratio, and the insensitivity of this ratio to the structure (and reactivity) of the silicon hydride [8,9]. It is also consistent with the magnitude of the solvent product isotope effects (PIE's). In fact, for the transition state (III) postulated for the closely analogous hydrolysis of pyridine—diphenylborane in acetonitrile, calculations [9] based on a B—H—H angle of 90° indicate that bond-orders of x of 0.3—0.5 for the forming H—H bond would give rise to k_{BH}/k_{BD} ratios of 1.5—1.2, and bond orders of 0.7—0.5 for the breaking H—O bond to k_{SH}/k_{SD} ratios of 4.1—4.5, and rather similar results could be expected for calculations based on (II).

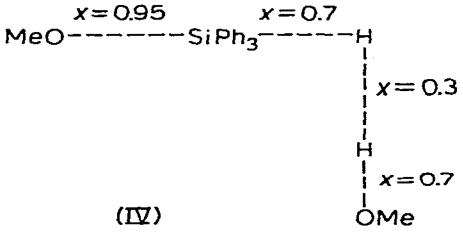
Structure (II) is also consistent with the observed solvent isotope effect on the overall rate, k_{SH}/k_{SD}, when account is taken of the greater availability of the methoxide ion in MeOD than in MeOH.

(3) It is consistent with variations in the PIE values with the electronic nature of the substituents attached to the silicon atom. The greater the electron-withdrawal from silicon by the R groups, the more stable will be the intermediate (I), the further the transition state (II) will be displaced from it towards the products [10], and so the smaller will be the O---H bond order, and the larger the PIE. The calculations [9] based on (III) indicate that the k_{OH}/k_{OD} isotope effect will vary from 2.9 for $x = 0.1$ to 4.5 for $x = 0.5$.

(4) It is reasonably consistent with the absence of significant catalysis by phenoxide ion, which, according to Schowen and his colleagues [2], indicates that the H---O bond order in the transition state is "greater than 0.7—0.8 (certainly greater than 0.5)".

The difference between the mechanism implied by the transition state (II) and that described by Schowen and his colleagues is largely one of emphasis, in that we would not subscribe to their view that the hydride ion "does not receive much assistance from electrophiles in the displacement from silicon by methoxide ion" [2]. While it does appear to be the case that the bond-order of the forming H---H bond may be only in the range 0.1—0.5 in the transition state, this bonding provides a very substantial degree of stabilization in the transition state, since separation of the free hydride ion would require a very large amount of energy. The importance of the proton transfer to the separating hydride ion is reflected clearly in the sensitivity of the solvent PIE to changes in the reactivity of the silicon hydride.

We should note at this point that we have adopted the two-step mechanism (1) because it accounts so simply for the increase in the magnitude of the solvent PIE as the reactivity of the silicon hydride is increased. For the single-step concerted process (2), Hammond's postulate [10] would suggest that increase in the reactivity of the hydride would result in a displacement of the transition state towards the reactants, and thus there would be a smaller degree of Si—H and H—OMe bond breaking, contrary to observation. However, the absolute rate theory holds that the rate of a reaction is determined by the free energy change between the initial state and the highest energy transition state, and (within a small factor) is unaffected by the existence of intermediates in the route to that transition state. It seems to us that the effects of substituents on a transition state such as (IV)*, should operate in the same direction as those in (II), which differs from (IV) only in that the bond-order of the MeO—Si bond is 1.0 rather than 0.95.



(IV)

---

*Structures (II) and (IV) are not intended to imply anything about the stereochemistry around the silicon atom.

If increased electron-withdrawal from silicon increases the H---H bond-order in transition state (II), we believe that it should do so also in (IV), in spite of the apparent conflict with the Hammond postulate. While the two-step process (1) certainly provides a conceptually simpler picture, it would be unwise to rely on the necessarily broad generalizations of the Hammond postulate [10] to rule out entirely the single-step concerted process (2).

The behaviour of tris(pentafluorophenyl)silane

The PIE for tris(pentafluorophenyl)silane in MeOH/MeOD/C_6H_6 containing 2*M* NaOMe is anomalous in that the observed value, viz. 3.98, is smaller than those found for the much less reactive $(p\text{-}ClC_6H_4)_3SiH$ and $(m\text{-}CF_3C_6H_4)_3SiH$. Extensive cleavage of the Si—C_6F_5 bonds certainly occurs, but this cannot account for the anomaly, since even if such cleavage precedes the reaction of the Si—H bond, the very highly reactive silicon hydride produced must still be giving rise to a smaller PIE than less reactive hydrides. Furthermore, in the much less basic medium consisting of MeOH/MeOD/C_6H_6 containing pyridine, in which there is probably less cleavage of the Si—C_6F_5 bonds, a similar PIE value is obtained. In principle, the low PIE could be accounted for by postulating that the intermediate is so stable in this case that the extent of the breaking of the H—OMe bond required in the transition state lies beyond the point of the maximum k_{SH}/k_{SD} primary isotope effect; the calculations [9] in the case of transition state (III) indicate, however, that the maximum does not occur until an H—H bond-order of about 0.8 is reached, and a k_{SH}/k_{SD} ratio of 3.98 would probably require an H—H bond-order of > 0.9. It may be that some entirely different mechanism is involved for this hydride, and it is noteworthy that hydrogen is generated rapidly when the silane is treated with MeOH/MeOD/C_6H_6 containing aqueous hydrogen chloride, and that the value of the PIE in this case, viz. 3.70, is very close to that observed for the basic solvolysis. It is relevant that Lappert and Lynch, when they first made this hydride, suggested that its reactions might differ in nature and not just rate from those of other triarylsilanes [11].

Experimental

Materials

The silicon hydrides were prepared by standard procedures from trichlorosilane and the appropriate Grignard reagent in ether, and purified by fractional distillation and/or recrystallization. The physical properties agreed with those given in the literature.

In the case of tris(pentafluorophenyl)silane, made from trichlorosilane, bromopentafluorobenzene, and magnesium in situ in ether under nitrogen, the product mixture was not, as was usual in the other cases, treated with aqueous ammonium chloride; instead, benzene was added, the ether was evaporated off, and the solids were removed by filtration. Evaporation of the benzene from the filtrate left a solid residue, which was sublimed (100°/ca. 0.01 mm) to give material of m.p. 131° (lit. [11], 133°). The product gave hydrogen on treatment with methanol, and the rate of gas evolution was markedly increased by addition of acid or base.

Triethyldeuteriosilane was prepared from bromotriethylsilane and lithium aluminium deuteride, and shown by mass spectrometry to contain about 90% of Et_3SiD and 10% of Et_3SiH.

The *O*-deuteriomethanol, supplied by Ryvan, was > 99% isotopically pure. A 2.0 *M* solution of sodium methoxide in 1/1 MeOH/MeOD was prepared by mixing 10.0 volumes of a 3.8 *M* solution of sodium methoxide in MeOH with 9.0 volumes of MeOD. (This medium contains essentially equimolar amounts of available protium and deuterium.)

Measurement of product isotope effects

A three-necked flask containing a magnetic stirrer bar was fitted with two delivery funnels and with a vessel, evacuated, and closed at both ends with vacuum-tight taps, suitable for attachment to the mass spectrometer. The flask was evacuated, and the MeOH/MeOD/MeONa mixture (5.0 ml) was run in from one funnel, and a solution (4.0 ml) of the silicon hydride (ca. 1.0 mmole) in anhydrous benzene was added rapidly (ca. 3 s) from the other with vigorous stirring. The mixture was stirred for 2 h at room temperature (21° ± 1°), and a sample of the hydrogen was then tapped off into the evacuated vessel. The H_2/HD ratio determined on an A.E.I. M.S.9 spectrometer at 20 eV by scanning the region to mass number 4 six times, measuring the peak heights, and averaging the ratios of peak heights for masses 2 and 3. The small background hydrogen peak was also measured and taken into account. The hydrogen background from the benzene—methanol mixture was also checked, but was always negligible.

In the case of triphenylsilane, the reaction was also carried out by adding a solution of the hydride in 1/1 MeOH/MeOD to an equal volume of a 2.0 *M* solution of NaOMe in 1/1 MeOH/MeOD.

In the case of tris(pentafluorophenyl)silane, after the hydrogen sample had been taken the solution was added to ice. Ether extraction, followed by GLC examination of the ethereal solution, revealed the presence of a substantial amount of pentafluorobenzene. The PIE was also measured for this silicon hydride by using, in place of the MeOH/MeOD/MeONa solution, (*i*) a solution of pyridine (0.5 *M*) in 1/1 MeOH/MeOD, or (*ii*) a solution of hydrochloric acid (1.0 ml of s.g. 1.16) in MeOD (4.0 ml). In each case pentafluorobenzene was detected in the products after the reaction mixture had been added to ice-water.

Acknowledgements

We thank Dr. D.R.M. Walton for valuable discussions, and Imperial Chemical Industries Limited, for the award of a Fellowship (to I.D.J.). Skilled technical assistance by Mr. A. Greenway and Mr. C. Simpson is also gratefully acknowledged.

References

1 C. Eaborn, Organosilicon Compounds, Butterworths, London 1960, pp. 200—204.
2 K. O'Donnell, R. Bacon, K.L. Chellappa, R.L. Schowen and J.K. Lee, J. Amer. Chem. Soc., 94 (1972) 2500.

3 L. Kaplan and K.E. Wilzbach, J. Amer. Chem. Soc., 77 (1955) 1297.
4 R.L. Schowen and R. Bacon, Tetrahedron Lett., (1970) 4177.
5 C.D. Ritchie and H.F. King, J. Amer. Chem. Soc., 90 (1968) 833.
6 L.H. Sommer, W.D. Korte and C.L. Frye, J. Amer. Chem. Soc., 94 (1972) 3463.
7 R.A. More O'Ferrall, Chem. Commun., (1969) 114; C.G. Mitton, M. Gresser and R.L. Schowen, J. Amer. Chem. Soc., 91 (1969) 2045.
8 E.S. Lewis and M.C.R. Symons, Quart. Rev., (1958) 230; M.F. Hawthorne and E.S. Lewis, J. Amer. Chem. Soc., 80 (1958) 4296; E.S. Lewis and R.H. Grinstein, ibid., 84 (1962) 1158; G.A. Olah, P.W. Westerman, V.K. Mo and G. Klopman, ibid., 94 (1972) 7859.
9 R.A. More O'Ferrall, J. Chem. Soc. B, (1970) 785.
10 G.S. Hammond, J. Amer. Chem. Soc., 77 (1955) 334.
11 M.F. Lappert and J. Lynch, Chem. Commun., (1968) 750.