calculations suggest only slight changes in bond energy for substantial deviation of linearity of the C–Zn–C axis.[34] The packing of the molecule is interesting and consists of chains along the *b* axis, with the metal centers located above the below the *bc* plane in alternate molecules (Figure 2). There are no particularly short or unusual contacts between the molecules.

There are no other adducts with which the coordination geometry at zinc in the present compound can be compared; however a molecule with the same set of donor atoms, bis(3-(dimethylamino)propyl)zinc, $[Zn((CH_2)_3N(Me)_2)_2]$, has been studied in some detail by electron diffraction in the vapor phase (GED) and in the solid state by x-ray diffraction.[34] Bond lengths and angles at zinc for $[Zn((CH_2)_3N(Me)_2)_2]$ are tabulated in Table V to allow easy comparison with those for the adduct prepared in the present study. In the present, stable, solid crystalline adduct, the Zn–N distance is much greater than the sum of the covalent radii and suggests little or no covalent interaction between the nitrogen and metal. The reported[34] range of Zn–N bond lengths was previously from 1.82 Å in $[Zn(N(SiMe_3)_2)_2]$ to 2.32 Å in $[Zn((CH_2)_3N(CH_3)_2)_2]$ and is now extended to 2.41 Å.

The zinc adduct with the trimethyltriazine has been successfully used,[18,21] in combination with H_2Se, to grow high-quality layers of ZnSe by conventional atmospheric pressure MOCVD experiments[18] (see Table VI). Thin films of ZnSe grown from this precursor are essentially fully depleted and free from n-type dopants (such as iodide) which adversely effect the properties of this material. One reason for this observation may be that the adduct is extremely effective in removing traces of MeI from dimethylzinc.

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Supplementary Material Available: Tables of atomic coordinates, temperature factors, bond lengths and angles, and nonbonded distances (3 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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(34) Dekker, J.; Boersma, J.; Fernholt, L.; Haaland, A.; Spek, A. L. *Organometallics* 1987, *6*, 1202.

Role of Pentacoordinate Intermediates in the Hydrolysis Reaction of Organic Silicates

R. J. P. Corriu,* C. Guerin, B. J. L. Henner, and Q. Wang

Laboratoire "Hétérochimie et Amino-acides", URA CNRS 1097, Université de Montpellier II, Sciences et Techniques du Languedoc, Place E. Bataillon, F-34095 Montpellier Cedex 5, France

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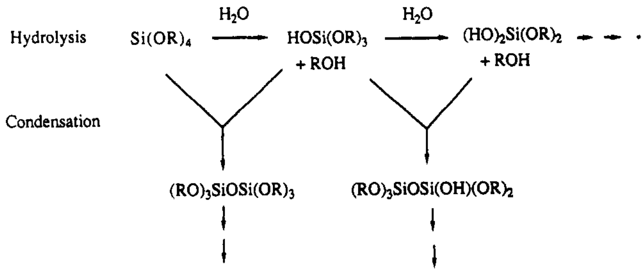
The alcoholysis and hydrolysis reactions of $XSi(OR)_3$, $XSi(OR)_3$ + 10% KOR (X = H, OR), and $K[XSi(OR)_4]$ (X = H) or $[K,18\text{-crown-}6][XSi(OR)_4]$ (X = OR) were studied to approach the mechanism of the reaction. We found the following: (i) The first step of the process in the case of $XSi(OR)_3$ (X = H, OR) was the formation of a pentacoordinate intermediate by nucleophilic activation at silicon. (ii) The rate-determining step was the coordination of R′OH (R′ = H, R) to the pentacoordinate silicon leading to a hexacoordinate intermediate (or transition state), which gave the product. (iii) A step by step nucleophilic substitution occurred on a pentacoordinate silicon derivative, $K[H_2Si(OR)_3]$ and $K[HSi(OR)_4]$, giving another pentacoordinate compound, $K[HSi(OR)_4]$ and $[K,18\text{-crown-}6][Si(OR)_5]$, respectively.

Introduction

The hydrolysis of organic silicates, mainly $Si(OMe)_4$ and $Si(OEt)_4$, is the key reaction in the sol–gel process for preparation of silica. The mechanism of this reaction is complex because of competition between hydrolysis, condensation reactions, and redistribution reactions. The different reactions in the hydrolysis process are summarized in Scheme I.

The mechanism of the hydrolysis of silicon alkoxides depends on the reaction conditions (neutral or catalyzed with acids, bases, or nucleophiles) and has been studied by several groups.[1-7]

Scheme I



In the case of basic conditions, two mechanisms may be envisaged. In the more common mechanism (Scheme II)

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(1) Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960. Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 2294. Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. *Ibid.* **1954**, *76*, 5190.

(2) Iler R. K. *The Chemistry of Silica*; Wiley: New York, 1979. Grubb, W. T. *J. Am. Chem. Soc.* **1954**, *76*, 3408. Assink, R. A.; Kay, B. D. *J. Non-Cryst. Solids* **1988**, *99*, 359; *Ibid.* **1988**, *104*, 112; *Ibid* **1988**, *107*, 35.

(3) Brinker, C. J. *J. Non-Cryst. Solids* **1988**, *108*, 31.

(4) Zerda, T. W.; Hoang, G. *J. Non-Cryst. Solids* **1989**, *109*, 9. *Ibid. Chem. Mater.* 1990, *2*, 372.

(5) For a general survey and statement, see: Brinker, C. J.; Scherer, G. W. *Sol Gel Science. The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990.

Scheme II

hydrolysis

$$HO^- + (RO)_3SiOR \xrightarrow{slow} (RO)_3SiOH + RO^-$$

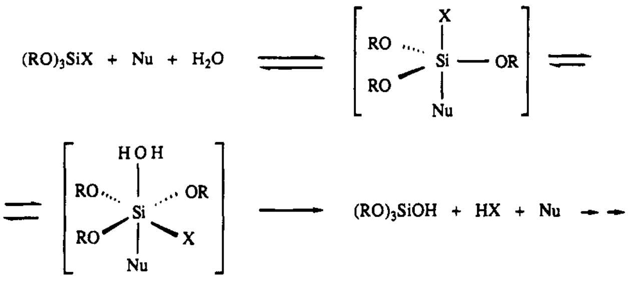
$$RO^- + H_2O \xrightarrow{fast} ROH + OH^-$$

condensation

$$(RO)_3SiOH + OH^- \xrightarrow{fast} (RO)_3SiO^- + H_2O$$

$$(RO)_3SiO^- + (RO)_4Si \xrightarrow{slow} (RO)_3SiOSi(OR)_3 + RO^-$$

Scheme III



Nu = F-,OH-,OR-,HMPA (hexamethylphosphoramide),NMI (N-methylimidazole), DMAP (dimethylaminopyridine).
X = leaving group: Cl,OR,H.

the hydrolysis reaction is considered a pure nucleophilic displacement at silicon. The increase of rate due to the catalyst corresponds to an increase of the nucleophilicity of the reagent, OH^- instead of H_2O (Scheme II).

However, another possible mechanism (Scheme III) is a nucleophilic activation, leading first to a pentacoordinate silicon intermediate;[8] the next step, which is the rate-determining step, is coordination of water, giving a hexacoordinate intermediate that leads to the products (Scheme III).

This mechanism assumes that the pentacoordinate intermediate is more reactive toward the substituting nucleophile (H_2O in this case) than the related tetracoordinate neutral derivative. This assumption has been proven in the studies of the reactivity of pentacoordinate silicon species.[9] For instance, we have prepared the phenylated pentacoordinate derivatives [K,18-crown-6][Ph_nSiX_{5-n}] (X = F, OMe); [K,18-crown-6][Ph_3SiF_2] reacted with a hindered Grignard reagent, *i*-PrMgBr, 150 times faster than Ph_3SiF. In the same manner, we have shown that the hydrolysis of [K,18-crown-6][$Ph_3Si(OMe)_2$] was faster than the hydrolysis of Ph_3SiOMe.[9c]

In order to check this hypothesis, we have considered the reactivity toward hydrolysis and alcoholysis of pentaalkoxosilicates, [K,18-crown-6][$Si(OR)_5$], and hydridoalkoxosilicates, K[$HSi(OR)_4$] and K[$H_2Si(OR)_3$], which have been prepared recently.[10] The electrophilicities of K[$HSi(OR)_4$] and K[$H_2Si(OR)_3$] have been proven.[10,11] For instance, these compounds reacted easily with Grignard reagents to give the substituted neutral derivatives with good yields. We also generally observed that these pentacoordinate silicon derivatives are more reactive toward nucleophiles than the corresponding tetracoordinate species.[9-11]

Table I. Hydrolysis of $Si(OR)_4$

entry	compound	reaction time	product aspect	IR anal.
1	$Si(OMe)_4$	7 h	liquid	$Si(OMe)_4$
2		5 days	viscous liquid	No $Si(OMe)_4$
3	$Si(OMe)_4$ + KOMe(cat)	3 h	liquid + some solid	mainly $Si(OMe)_4$
4		7 h	liquid + some solid	$Si(OMe)_4$ minor
5	[K,18-crown-6]-[$Si(OMe)_5$]	<1 min	white precipitate	
6	$Si(OEt)_4$	7 days	liquid	$Si(OEt)_4$
7	$Si(OEt)_4$ + KOEt(cat)	4 h	liquid	$Si(OEt)_4$
8		4 days	liquid	$Si(OEt)_4$ + some SiOSi
9	[K,18-crown-6]-[$Si(OEt)_5$]	2–3 h	early stage of gelification	no $Si(OEt)_4$
10	$Si(OPh)_4$	5 days	early stage of gelification	$Si(OPh)_4$ minor
11	$Si(OPh)_4$ + KOPh (cat)	40 min	white precipitate	no $Si(OPh)_4$
12	[K,18-crown-6]-[$Si(OPh)_5$]	<1 min	gel	no $Si(OPh)_4$

These facts are corroborated by calculations[12,13] showing that the silicon atom is still electropositive in the pentacoordinate compound. Moreover, the lengthening of the bonds on going from a tetrahedron to a trigonal bipyramid may explain the higher reactivity of the pentacoordinate silicon compound.

In this paper we report the study of the hydrolysis and alcoholysis reactions of the pentacoordinate species [K,18-crown-6][$Si(OR)_5$] and K[$HSi(OR)_4$] (R = Me, Et, *i*-Pr, Ph) by comparison to the hydrolysis of tetracoordinate silicates.

Results and Discussion

We first studied the hydrolysis reaction of the pentaalkoxosilicates [K,18-crown-6][$Si(OR)_5$]. These derivatives were prepared previously[9,14] according to the Damrauer procedure[15] (eq 1).

$$Si(OR)_4 + KOR + 18\text{-crown-6} \rightarrow [K,18\text{-crown-6}][Si(OR)_5] \quad (1)$$

$$R = Me, Et, n\text{-}Bu, Ph$$

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[6] Corriu, R. J. P.; Leclercq, D.; Vioux, A.; Pauthe, M.; Phalippou, J. In *Ultrastructure Processing and Advanced Ceramics*; Mackenzie J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988. Corriu, R. J. P.; Young, J. C. In Hypervalent Silicon Compounds. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 20, p 1241. Belot, V.; Corriu, R.; Guérin, C.; Henner, B.; Leclercq, D.; Mutin, H.; Vioux, A.; Wang, Q. *Better Ceramics Through Chemistry IV*; Materials Research Society: Pittsburgh, 1990; pp 3–14.

[7] Keefer, K. D. *Mater. Res. Soc. 32*, **1985**, 15.

[8] Corriu, R. J. P.; Dabosi, G.; Martineau, M.; *J. Organomet. Chem.* **1978**, *150*, 27; *Ibid.* **1978**, *154*, 33; *Ibid.* **1980**, *186*, 25.

[9] (a) Corriu, R. J. P. Hypervalent Silicon Compounds. 8th International Symposium on Organosilicon Chemistry, June 7–12, 1987, St. Louis, MO. (b) Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1988**, *7*, 237. (c) Brefort, J. L.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallic* **1990**, 9, 256.

[10] Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *359*, C33. Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *Organometallics*, accepted for publication.

[11] Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *368*, C25.

[12] Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378. Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760. Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601. Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056.

[13] Deiters, J. A.; Holmes, R. R. Poster 31, ACS Silicon Meeting, Philadelphia, PA, April 1989. *Idem. J. Am. Chem. Soc.* **1990**, *112*, 7197.

[14] Kumara Swamy, K. C.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2341.

Under basic conditions, the possible nucleophilic activation by OH^- (Scheme III) involves the formation of a pentacoordinate silicate during the first step followed by the nucleophilic attack of water at silicon acting as an electrophilic center. Furthermore, the mechanism implies that this last step must be faster than the hydrolysis of the starting tetraalkoxysilane.

In order to verify this hypothesis, we have studied the hydrolysis and gel times of the isolated pentaalkoxosilicates $[K,18\text{-crown-}6][Si(OR)_5]$ (R = Me, Et, Ph) and compared them to $Si(OR)_4$ and $Si(OR)_4$ catalyzed with 10% KOR (R = Me, Et, Ph). The results are summarized in Table I.

Hydrolysis of $Si(OMe)_4$ is known to be slow;[5] in dilute solution (0.1 M) (Table I, entry 1), no evolution of the mixture was observed after 7 h. The infrared spectrum showed $Si(OMe)_4$ as a unique product. After 5 days (Table I, entry 2) a more viscous solution was obtained. The infrared spectrum indicated SiOMe (2845 cm^{-1}) and SiOSi (800, 1020 cm^{-1}) absorption bands, but no starting material, $Si(OMe)_4$, was present. When 10% KOMe was added (Table I, entries 3 and 4), the infrared spectrum gave $Si(OMe)_4$ as the main compound after 3 h, but a shoulder appeared at 1020 cm^{-1} corresponding to SiOSi bonds. After 7 h, the reaction has evolved and $Si(OMe)_4$ was the minor compound of the mixture. By contrast, the pentacoordinate compound $[K,18\text{-crown-}6][Si(OMe)_5]$ (Table I, entry 5) gave a very fast hydrolysis reaction; a white precipitate was obtained immediately.

A similar set of results was obtained in the case of $Si(OEt)_4$, except that the rates of the reactions were much slower. Indeed, no evolution was observed in the case of $Si(OEt)_4$ after 7 days at room temperature (Table I, entry 6) or after 4 h with KOEt as catalyst (Table I, entry 7); moreover, some evolution was observed after 4 days (Table I, entry 8) by the appearance in the infrared spectrum of a shoulder at 1020 cm^{-1} corresponding to SiOSi bonds. The pentacoordinate species itself, $[K,18\text{-crown-}6][Si(OEt)_5]$, was more easily hydrolyzed (Table I, entry 9); the early stage of gelification was observed after 2–3 h of reaction. More interesting are the results obtained with the phenoxy compounds (Table I, entries 10–12); the early stage of gelification was observed in the hydrolysis of $Si(OPh)_4$ after 5 days of reaction. When a catalytic amount of KOPh (10%) was added (Table I, entry 11), a monolithic gel was obtained after 40 min. Finally, with $[K,18\text{-crown-}6][Si(OPh)_5]$ (Table I, entry 12), the gel was obtained immediately.

In conclusion, the neutral tetracoordinated silicon derivatives $Si(OR)_4$ (R = Me, Et, Ph) were difficult to hydrolyze under neutral conditions. As observed previously, the reaction was faster when a catalytic amount of KOR was added. These results could be interpreted by a base-catalyzed reaction (see Scheme II). However, the acceleration observed in the case of $Si(OPh)_4$ + 10% KOPh (Table I, entry 11) compared to $Si(OPh)_4$ (Table I, entry 10) cannot be interpreted in terms of basicity. Indeed, PhO^- is less basic than EtO^- but reacted faster. This suggested that RO^- acted as a coordinating agent in these reactions. Moreover, in agreement with that, we have observed that all isolated pentacoordinate silicates (Table I, entries 5, 9, and 12) were much more easily hydrolyzed than the tetravalent analogues (Table I, entries 1, 6, and 10).

However, during the hydrolysis of $Si(OR)_4$ and $[K,18\text{-crown-}6][Si(OR)_5]$, it was not possible to isolate any intermediate and have by this way real proof of the proposed mechanism. This is the reason why we have studied the hydride family, $HSi(OR)_3$, $K[HSi(OR)_4]$, and $K[H_2Si(OR)_3]$, which contain two different substituents at silicon: H and OR. These two leaving groups are expected to react differently with alcohol or water and could provide some information on the mechanism of the reaction.

Table II. ^{29}Si NMR[a] Data for $[K,18\text{-crown-}6][Si(OR)_5]$ (δ)

$[K,18\text{-crown-}6][Si(OMe)_5]$	−127.7
$[K,18\text{-crown-}6][Si(OEt)_5]$	−131.3
$[K,18\text{-crown-}6][Si(On\text{-}Bu)_5]$	−130.0
$[K,18\text{-crown-}6][Si(OPh)_5]$	−148.3

[a] Solvent THF + 10% C_6D_6.

At first we studied the alcoholysis reactions; since the reactivities of Si–H bonds in pentacoordinate compounds have been evidenced previously,[10] we could expect nucleophilic displacement of the Si–H bond by the alcohol leading to pentaalkoxysilicates (eq 2).

$$K[HSi(OR)_4] + ROH + 18\text{-crown-}6 \rightarrow H_2 + [K,18\text{-crown-}6][Si(OR)_5] \quad (2)$$

$$R = Me, Et, n\text{-}Bu, Ph$$

In order to isolate in good condition the expected pentaalkoxysilicate formed during the process, the reactions were performed in the presence of 18-crown-6. This crown ether, known to stabilize the potassium salts of the pentacoordinate siliconates $K[R_nSiX_{5-n}]$ (X = F, OMe),[9,15] facilitates the isolation of the products.

The expected products were easily obtained in the case of R = Me, Et, *n*-Bu, and Ph. Table II gives the ^{29}Si NMR data obtained for the pentacoordinate silicon species. The chemical shifts are in good agreement with those obtained by Holmes et al.[14] using potassium alkoxide and tetraalkyloxysilane in the presence of 18-crown-6 (eq 1).

No pentacoordinate silicon complex was observed when the reaction was performed without crown ether (eq 3).

$$[HSi(OR)_4]K + ROH \xrightarrow[78\ ^\circ C \rightarrow rt]{THF} H_2 + Si(OR)_4 + KOR \quad (3)$$

In this case, hydrogen evolved very quickly and after 1 h the main compound observed was $Si(OR)_4$; we assume that the transient pentacoordinate species $K[Si(OR)_5]$ is very unstable and decomposes into $Si(OR)_4$ and KOR (eq 3).

In conclusion, as illustrated in eq 2, a nucleophilic substitution occurred with $K[HSi(OR)_4]$ and alcohol leading to a new pentacoordinated silicon derivative. The latter can be isolated in the presence of crown ether. Moreover, $HSi(OR)_3$ itself did not react with alcohols. These two results confirm our hypothesis of the hydrolysis mechanism going through a pentacoordinate intermediate (Scheme III).

The mechanism of the alcoholysis reaction was well demonstrated with dihydridosilicates. Indeed, $K[H_2Si(O\text{-}i\text{-}Pr)_3]$ reacted with 1 equiv of 2-propanol to give the substitution of one hydride (eq 4), leading to another pentacoordinate derivative.

$$K[H_2Si(O\text{-}i\text{-}Pr)_3] + HO\text{-}i\text{-}Pr + 18\text{-crown-}6 \rightarrow [K,18\text{-crown-}6][HSi(O\text{-}i\text{-}Pr)_4] \quad (4)$$

This reaction is quantitative and shows that it is possible to replace only one hydride of the molecule. It must be underlined that this reaction also occurred without 18-crown-6; $K[HSi(Oi\text{-}Pr)_4]$ is stable without crown ether.[10]

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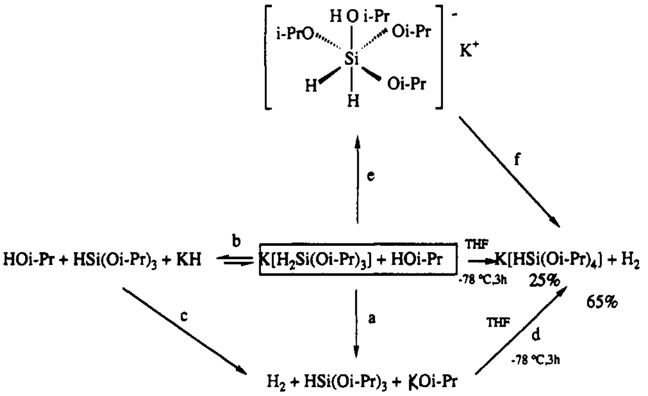
[15] Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

Table III

entry	starting materials	gelification time	aspect	product (IR, cm^{-1})
1	$HSi(OMe)_3$	5 days	liquid + gel[a]	Si–H (2254)
2	HSi(OMe) + KOMe (10%)	<1 min	powder	no SiH
3	$K[HSi(OMe)_4]$	<1 min	powder	no SiH
4	$HSi(OEt)_3$	5 days	viscous liquid[b]	Si–H (2252)
5	$HSi(OEt)_3$ + KOEt (10%)	1 h	gel	no SiH
6	$K[HSi(OEt)_4]$	13 min	gel	no SiH
7	$HSi(O\text{-}n\text{-}Bu)_3$	5 days	liquid	SiH (2245)
8	$HSi(O\text{-}n\text{-}Bu)_3$ + KO-*n*-Bu (10%)	15 h	gel	no SiH
9	$K[HSi(O\text{-}n\text{-}Bu)_4]$	2 h	gel	no SiH
10	$HSi(O\text{-}i\text{-}Pr)_3$	5 days	liquid[c]	SiH (2238)
11	$HSi(O\text{-}i\text{-}Pr)_3$ + KO-*i*-Pr (10%)	7 days	viscous liquid[d]	no SiH
12	$K[HSi(O\text{-}i\text{-}Pr)_4]$	30 h	gel	no SiH
13	$HSi(OPh)_3$	7 days	gel	traces of SiH (2243)
14	HSi(OPh) + KOPH (10%)	20 min	gel	no SiH
15	$K[HSi(OPh)_4]$	3 min	gel	no SiH

[a] Hydrogen titration gave 90% of recovered SiH. [b] Hydrogen titration gave 98% recovered SiH. [c] Pure starting material. [d] Small amounts of solid present.

Scheme IV[a]



[a] In order to follow easily the reaction of Scheme IV, we have found that HCl gas reacted with $K[H_2Si(O\text{-}i\text{-}Pr)_3]$ and $K[HSi(O\text{-}i\text{-}Pr)_4]$ to give $HSi(O\text{-}i\text{-}Pr)_3$ and $Si(O\text{-}i\text{-}Pr)_4$, respectively (vide infra, Scheme V).

This reaction is interesting from a mechanistic point of view since it can be explained in two ways: The first is an acid–base reaction (Scheme IV, step a) or dissociation process (Scheme IV, steps b and c) followed by formation of the pentacoordinate hydrido alkoxo derivative (Scheme IV, step d). The second corresponds to nucleophilic attack at silicon through a hexacoordinated intermediate (Scheme IV, steps e and f).

In order to discriminate between these two mechanisms, we have performed the reaction at low temperature (−78 °C). In the case of the acid–base mechanism, the first step (Scheme IVa) must be relatively temperature independant and step d can be performed separately. We have compared the results obtained in the alcoholysis reaction in one part and in the reaction of step d in the other part. The reaction of $K[H_2Si(O\text{-}i\text{-}Pr)_3]$ and 2-propanol at −78 °C gave, after 3 h, 25% yield of $K[HSi(O\text{-}i\text{-}Pr)_4]$. Under the same experimental conditions, the reaction of $HSi(O\text{-}i\text{-}Pr)_3$ and KO-*i*-Pr (Scheme IV, step d) gave 65% yield of $K[HSi(O\text{-}i\text{-}Pr)_4]$; the reaction is fast even at −78 °C compared to the alcoholysis reaction of $K[H_2Si(O\text{-}i\text{-}Pr)_3]$. This fact demonstrated that the alcoholysis does not correspond to an acid–base reaction followed by the recombination of potassium isopropoxide with triisopropoxysilane. The most convincing mechanism corresponds to the formation of a hexacoordinate intermediate (Scheme IV, steps e and f) resulting from attack of the alcohol at silicon.

All the reactions products of Scheme IV were analyzed by gas chromatography after treatment with HCl gas. Scheme V summarizes these reactions, which have been carried out separately.

Scheme V

$$HSi(O\text{-}i\text{-}Pr)_3 + HCl(g) \xrightarrow[-78\ ^\circ C,\ 10\ min]{THF} HSi(O\text{-}i\text{-}Pr)_3 + \text{trace } Si(O\text{-}i\text{-}Pr)_4$$

$$K[HSi(O\text{-}i\text{-}Pr)_4] + HCl(g) \xrightarrow[-78\ ^\circ C,\ 10\ min]{THF} Si(O\text{-}i\text{-}Pr)_4 + H_2 + KCl$$

$$K[H_2Si(O\text{-}i\text{-}Pr)_3] + HCl(g) \xrightarrow[-78\ ^\circ C,\ 10\ min]{THF} \underset{75\%}{HSi(O\text{-}i\text{-}Pr)_3} + \underset{12\%}{Si(O\text{-}i\text{-}Pr)_4} + H_2 + KCl$$

We observed that $HSi(O\text{-}i\text{-}Pr)_3$ was not affected by HCl and that the hydrido pentacoordinate species reacted specifically with HCl; $K[HSi(O\text{-}i\text{-}Pr)_4]$ gave $Si(O\text{-}i\text{-}Pr)_4$ and $K[H_2Si(O\text{-}i\text{-}Pr)_3]$, mainly $HSi(O\text{-}i\text{-}Pr)_3$. Thus, the reaction with HCl allows easy analysis of a mixture of $K[H_2Si(O\text{-}i\text{-}Pr)_3]$ and $K[HSi(O\text{-}i\text{-}Pr)_4]$.

To conclude the discussion of the alcoholysis reactions of hydridosilicates, we have demonstrated that the reaction occurred step by step, going from a pentacoordinate compound to another pentacoordinate derivative (Scheme VI) by nucleophilic substitution at silicon.

Scheme VI

$$K[H_2Si(OR)_3] \xrightarrow{ROH} K[HSi(OR)_4] \xrightarrow[18\text{-crown-}6]{ROH} [K,18\text{-crown-}6][Si(OR)_5]$$

From a mechanistic point of view, the rate-determining step is the coordination of the alcohol to the silicon leading to a new pentacoordinate species through a hexacoordinate intermediate or transition state.

These observations might also be applied to the mechanism of the hydrolysis reaction of $K[HSi(OR)_4]$ and $[K,18\text{-crown-}6][Si(OR)_5]$; it is why we have studied the hydrolysis reactions using three different conditions: (i) the neutral derivatives $HSi(OR)_3$ (R = Me, Et, *n*-Bu, *i*-Pr, Ph); (ii) the neutral derivatives plus a catalytic amount of the corresponding alkoxide KOR; (iii) the preformed pentacoordinate silicon derivative $K[HSi(OR)_4]$. All these reactions were performed in THF as solvent with the same substrate and water concentrations. Table III is a summary of the results obtained with the hydride derivatives.

To obtain a gel with $HSi(OR)_3$ (R = Me, Et), the hydrolysis reactions are usually performed at high concentrations.[5,16] Under neutral conditions the gel obtained showed that the Si–H bond was not affected. Under basic conditions, hydrogen evolved immediately and gave a gel without a Si–H bond. In order to be able to compare our results in the hydrolysis of the pentacoordinate and tetracoordinate silicon derivatives, we used dilute solutions (0.1 M).

Table III shows that the hydrolysis of $HSi(OR)_3$ (R = Me, Et, *n*-Bu, *i*-Pr, Ph) is generally slow and depends on the R group (Table III, entries 1, 4, 7, 10, and 13). For instance, $HSi(OMe)_3$ (Table III, entry 1) gave a mixture of liquid and gel after 5 days at room temperature; but with R = Et or *n*-Bu (Table III, entries 4 and 7), $HSi(OR)_3$ gave a more viscous solution, indicating only a small change in the medium. With the more hindered isopropyl group (Table III, entry 10) no change was observed after 5 days at room temperature. As expected, the IR spectra of these derivatives showed that the Si–H bond was still present; moreover, hydride titration (cf. Experimental Section) in the case of R = Me and Et gave 90 and 98%, respectively, recovered hydrogen. This means that, under neutral conditions,[16] hydrolysis of SiOR occurred before hydrolysis of Si-H. On the other hand, electronic factors are also important in the hydrolysis reactions. A gel was obtained in the case of $HSi(OPh)_3$ (Table III, entry 13), after 7 days of reaction at room temperature. In this case, IR analysis gave only traces of Si–H, indicating that this bond was hydrolyzed. The observed order of hydrolysis, under neutral conditions is $HSi(OPh)_3 > HSi(OMe)_3 > HSi(OEt)_3$, $HSi(O\text{-}n\text{-}Bu)_3 > HSi(O\text{-}i\text{-}Pr)_3$.

It is well-known that the hydrolysis of alkoxysilanes is catalyzed with bases; addition of 10% of the corresponding KOR to the trialkoxysilanes greatly favors gel formation (Table III, entries 2, 5, 8, 11, and 14). For instance (Table III, entry 5), immediate gas evolution and formation of a solid along the wall of the tube was observed with $HSi(OEt)_3$ + 10% KOEt. The IR spectrum showed no Si–H bond in the product. If no hydrolysis was observed in the case of $HSi(O\text{-}i\text{-}Pr)_3$ after 5 days (Table III, entry 10), addition of KO-*i*-Pr gave immediate evolution of hydrogen but no gelification. However, after 10 days at room temperature, the medium had two components: a liquid phase corresponding to the siloxane, $(i\text{-}PrO)_3SiOSi(O\text{-}i\text{-}Pr)_3$, identified by mass spectroscopy, and a film of gel along the wall of the Schlenk tube. With a phenoxy group (Table III, entry 14), the gel time was 20 min. In the case of pentacoordinate hydridosilicates $K[HSi(OR)_4]$ (Table III, entries 3, 6, 9, 12, and 15), the formation of a gel was observed whatever the R group. In all cases, immediate evolution of hydrogen was observed. Indeed, the rate of formation of the gel was always faster compared to $HSi(OR)_3$ or $HSi(OR)_3$ + KOR (10%); for instance, with the phenoxy derivatives (Table III, entries 13–15) the gel was formed in 1 week from pure hydrosilane but needed only 20 min when 10% KOPh was added and about 3 min to be formed from $K[HSi(OPh)_4]$.

The gel formed in the cases of $HSi(OEt)_3$ + KOEt (10%) (Table III, entry 5) and $K[HSi(OEt)_4]$ (Table III, entry 6) was partially dried under vacuum (40–50 °C (0.5 mmHg)) leading to white powders; solid-state ^{29}Si NMR showed a signal at −84.8 ppm for the gel obtained from $K[HSi(OEt)_4]$ and a signal at −96.0 ppm in the case of $HSi(OEt)_3$ + KOEt (10%). This result shows that the structures of the gels are different. In the latter case, the structure is closer to SiO_2 (−100 to 110 ppm) than in the case of the hydrolysis of $K[HSi(OEt)_4]$. This result may be expected from studies of Engelhardt et al.[17] on sodium silicates solutions with varying Na/Si ratios. This author found, using ^{29}Si NMR, that the degree of polymerization of the solutions was lower when Na/Si is high (>1) than for Na/Si <1. This corresponds to our results: When K/Si = 1, we observed a NMR signal at lower field than when K/Si = 0.1.

In conclusion, the facts observed supported the mechanism we have proposed for nucleophilic (F^-, NMI) and basic (OH^-) activation of hydrolysis of tetracoordinate silicates (Scheme III). We have found the following: (i) Anionic pentacoordinate silicon compounds react faster than the corresponding tetracoordinate derivatives in hydrolysis and alcoholysis reactions, as was observed previously in the case of other nucleophilic substitutions.[9,10] (ii) The hydrolysis reaction is a nucleophilic rather than a base-catalyzed process. (iii) The nucleophilic displacement taking place on a pentacoordinate silicon involves the formation of a hexacoordinate intermediate (or transition state) by coordination of a molecule of H_2O (or ROH). (iv) The alcoholysis reaction occurred step by step, going from a pentacoordinate silicon derivative to another pentacoordinate compound by substitution of one ligand.

Experimental Section

All reactions were carried out under argon with use of a vacuum line and Schlenk tubes. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled before use. Methanol and ethanol were distilled over magnesium; 2-propanol was distilled, and phenol was used as received. $HSi(O\text{-}i\text{-}Pr)_3$ was prepared from $HSiCl_3$ and 2-propanol in pentane in the presence of triethylamine. The same procedure was used in the preparation of $HSi(OPh)_3$ but with diethylaniline as the HCl trapping agent. The following compounds were purchased: $Si(OMe)_4$, $HSi(OEt)_3$ (Fluka), $HSi(OMe)_3$, $Si(OEt)_4$ (Aldrich). KOR (R = Me, *i*-Pr, Ph) was prepared from KH and the corresponding alcohol in THF as solvent. $K[HSi(OR)_4]$ (R = Me, Et, *n*–Bu, Ph) and $K[H_2Si(O\text{-}i\text{-}Pr)_3]$ were prepared according to published procedures.[10,11]

IR spectra were recorded with a Perkin-Elmer 1600 FT instrument. ^{29}Si NMR spectra were recorded on a Brucker AC-250 (solution) or Brucker AM 300 (solid) and are referenced to tetramethylsilane. Gas chromatography analysis were performed on a Delsi 30 chromatograph using a 1.4-m-long 10% SE 30 column with temperature programming from 100 to 150 °C at a rate of 10 °C/mn.

Hydrolysis Reactions. $Si(OR)_4$ (R = Me, Et, Ph). The following procedure is given as an example. H_2O (0.045 g, 2.5 mmol) was added via syringe to a solution of $Si(OR)_4$ (1 mmol) in THF (10 mL). The mixture was kept at room temperature under the conditions in Table I. THF was removed under vacuum, and the viscous residue was analyzed by IR spectroscopy as a film with use of NaCl windows (see Table I). In the case of R = Ph, the gel was filtered and dried under vacuum. The IR spectrum (KBr pellet) gave a strong band at 1231 cm^{-1} and a medium one at 970 cm^{-1} corresponding to the Si–OPh stretching frequency (these bands are very strong in the case of $Si(OPh)_4$) and a broad band appeared at 1100 cm^{-1} corresponding to the SiOSi stretching frequency.

$Si(OR)_4$ + KOR (Catalytic) (R = Me, Et, Ph). A solution of KOR (0.1 mmol) and $Si(OR)_4$ (1 mmol) in 10 mL of THF was stirred for 5–10 min, and H_2O (0.045 g, 2.5 mmol) was then added via syringe. The mixture was kept at room temperature under the conditions in Table I. After filtration (R = Me, Et), the filtrate was evaporated under vacuum to give an oil that was analyzed by IR (neat, NaCl windows). The white precipitate obtained in the case of R = Ph was dried under vacuum and analyzed by IR (KBr pellet). The main broad band centered at 1100 cm^{-1} corresponds to the SiOSi frequency, and shoulders are observed at 1230 and 970 cm^{-1} characteristic of a SiOPh bond.

[K,18-crown-6][$Si(OR)_5$] (R = Me, Et, Ph). To a mixture of 1 mmol of $K[HSi(OR)_4]$ and 1 mmol of 18-crown-6 in THF (8

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[16] Belot, V.; Corriu, R. J. P.; Leclercq, D.; Mutin, H.; Vioux, A. *Chem. Mater*, in press.

[17] Engelhardt, G.; Michel, D. *High Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: New York, 1987.

mL) was added 1 mmol of the corresponding alcohol (ROH), and the reaction was stirred at room temperature for 1 h. A solution of H_2O (0.045 g, 2.5 mmol) in 2 mL of THF was added via syringe. The formation of a gel was observed rapidly; in the case of [K,18-crown-6][$Si(OMe)_5$], a white precipitate was observed (see Table I). The IR spectrum shows the SiOSi stretching frequency (1100 cm^{-1}) with shoulders at 970 and 1230 cm^{-1} characteristic of a SiOPh bond.

$HSi(OR)_3$ (R = Me, Et, *n*-Bu, *i*-Pr, Ph). H_2O (0.045 g, 2.5 mmol) was added neat via syringe to the solution of $HSi(OR)_3$ (1 mmol) in THF (10 mL). The solution was kept at room temperature without stirring under the conditions of Table III. The solvent was removed under vacuum to give a viscous liquid. IR spectra were recorded neat as a film with use of NaCl windows. (A KBr pellet was used in the case of the hydrolysis product of $HSi(OPh)_3$). See Table III.

$HSi(OR)_3$ + KOR (10%) (R = Me, Et, *n*-Bu, *i*-Pr, Ph). A 0.1-mmol portion of KOR was added to 5 mL of THF, and the mixture was stirred for 5 min. The solution was then added to the solution of the corresponding trialkoxysilane $HSi(OR)_3$ (1 mmol) and H_2O (0.045 g, 2.5 mmol) in THF (5 mL). The mixture was kept at room temperature under the conditions of Table III. IR spectra (KBr pellet) were recorded after evaporation of the solvent under vacuum.

K[$HSi(OR)_4$] (R = Me, Et, *n*-Bu, *i*-Pr, Ph). A solution of H_2O (0.045 g, 2.5 mmol) in THF (2 mL) was added to a solution of K[$HSi(OR)_4$] (1 mmol) in THF (8 mL), and the mixture was kept at room temperature without stirring under the conditions of Table III. IR spectra of the products were recorded after evaporation of the solvent under vacuum (KBr pellet). See Table III.

Alcoholysis Reaction of K[$HSi(OR)_4$] (R = Me, Et, *n*-Bu, Ph). To a solution of K[$HSi(OR)_4$] (8.0 mmol) and 18-crown-6 (8.0 mmol) in THF (20 mL) at 0 °C was added the corresponding alcohol ROH (8 mmol), neat, and the reaction mixture was stirred at room temperature for 1 h. Removal of the solvent under vacuum gave a white-yellow solid. ^{29}Si NMR spectral data are given in Table III. Data are identical with those for [K,18-crown-6][$Si(OR)_5$].[14]

Hydrogen Titration. After Hydrolysis of $HSi(OEt)_3$. The viscous liquid obtained after reaction of 1 mmol of $HSi(OEt)_3$ and evaporation of THF was dissolved in 5 mL of THF of a Schlenck tube, and 0.1 g of solid KOH was added. Gas evolution was measured with a gas buret over water. The reaction needs 20 min for 22 mL of gas while 98% (0.98 mmol) was obtained.

After Hydrolysis of $HSi(OMe)_3$. The same procedure as for the hydrolysis of $HSi(OEt)_3$ was used starting form 0.5 mmol of $HSi(OMe)_3$. Reaction time was 20 min. Ten milliliters of gas was obtained (0.045 mmol, 90%).

Reaction with HCl(g). To a solution of K[$H_2Si(O$-*i*-$Pr)_3$], K[$HSi(O$-*i*-$Pr)_4$], or $HSi(O$-*i*-$Pr)_3$ (1 mmol) in THF (10 mL) at −78 °C was bubbled HCl gas (dried through H_2SO_4) for 10 min. The excess HCl was pumped off immediately at low temperature, and the products were analyzed by gas chromatography. The results are given in Scheme V. The same procedure was used to follow the reactions of Scheme IV.

K[$H_2Si(O$-*i*-$Pr)_3$] + *i*-PrOH. A solution of *i*-PrOH (0.22 g, 3.7 mmol) in 5 mL of THF was added rapidly to a solution of K[$H_2Si(O$-*i*-$Pr)_3$] (0.90 g, 3.7 mmol) in THF (15 mL) at −78 °C. The mixture was stirred at −78 °C for 3 h and then treated with HCl gas at −78 °C. Gas chromatographic analysis gave 25% $Si(O$-*i*-$Pr)_4$ and 60% $HSi(O$-*i*-$Pr)_3$.

$HSi(O$-*i*-$Pr)_3$ + KO-*i*-Pr. A solution of $HSi(O$-*i*-$Pr)_3$ (0.32 g, 1.5 mmol) in THF (1 mL) was added rapidly to a solution of KO-*i*-Pr (0.15 g, 1.5 mmol) in THF (9 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and then treated with HCl gas at −78 °C. Gas chromatographic analysis gave 65% $Si(O$-*i*-$Pr)_4$ and 25% $HSi(O$-*i*-$Pr)_3$.

Synthesis of Stable Boryl-Substituted Diazomethane and Nitrilimines

Marie-Pierre Arthur,[†] Helen P. Goodwin,[‡] Antoine Baceiredo,[†] Keith B. Dillon,[‡] and Guy Bertrand*[,†]

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne,
31077 Toulouse Cédex, France, and Department of Chemistry, University of Durham,
Durham DH1 3LE, Great Britain

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Addition of bis(diisopropylamino)chloroborane to the lithium salt of (triisopropylsilyl)-, [bis(diisopropylamino)phosphino]-, and [bis(diisopropylamino)thioxophosphoranyl]diazomethane led to the corresponding stable *N*-borylnitrilimines **6**–**8** in 80, 90, and 95% yield, respectively. Addition of sulfur to C-phosphinonitrilimine **7** gave the thioxophosphoranyl analogue **8**. The chloroborane reacted with the lithium salt of diazomethane, leading to a mixture of [bis(diisopropylamino)boryl]diazomethane (**11**) (54% yield) and bis[bis(diisopropylamino)boryl]nitrilimine (**9**) (20% yield). Compound **9** can be obtained in good yield by reacting the lithium salt of [bis(diisopropylamino)boryl]diazomethane with chloroborane. Photolysis of nitrilimines **6**–**9** afforded the corresponding carbodiimides **12**–**15**. The regioselectivity and stereoselectivity of the 2 + 3 cycloaddition reactions of **6**–**8** with olefins were studied.

Introduction

Main-group element-substituted diazo compounds have been widely studied[1] except in the boron series. Indeed, only two examples of α-boryldiazomethane, characterized by IR in solution, have been reported.[2] The lack of examples in this class of compounds is probably due to the ability of Lewis acids to catalyze the decomposition of diazo derivatives.[1] Moreover, very little is known among the possible structural isomers of α-boryldiazo derivatives. To the best of our knowledge, a few borylcarbodiimides

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[†] Laboratoire de Chimie de Coordination du CNRS.

[‡] University of Durham.

[1] For reviews, see: (a) Patai, S. *The Chemistry of Diazonium and Diazo Groups*; Wiley: New York, 1978. (b) Regitz, M. *Diazoalkanes*; Georg Thieme Verlag: Stuttgart, 1977. (c) Regitz, M.; Maas, G. *Top. Curr. Chem.* **1981**, *97*, 71. (d) Regitz, M.; Maas, G. *Diazo Compounds, Properties and Synthesis*, Academic Press: Orlando, FL, 1986.

[2] (a) Tapper, A.; Schmitz, T.; Paetzold, P. *Chem. Ber.* **1989**, *122*, 595. (b) Schöllkopf, U.; Banhidai, B.; Frasnelli, H.; Meyer, R.; Beckhaus, H. *Liebigs Ann. Chem.* **1974**, 1767.

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