Journal of Organometallic Chemistry, 405 (1991) 173–177
Elsevier Sequoia S.A., Lausanne

JOM 21331

A contribution to the silicenium ion debate

Colin Eaborn

School of Chemistry and Molecular Sciences, University of Sussex, Brighton (UK)

(Received August 10th, 1990)

Abstract

It is suggested that the fact that $(Me_3Si)_3CSiMe_2OClO_3$ undergoes solvolysis fairly slowly in MeOH, and very slowly, if at all, in CF_3CH_2OH, argues strongly against the view that triorganosilyl perchlorates are significantly ionized in dichloromethane or sulpholane. Brief comments are made on aspects of some reactions that may involve silicenium ions as intermediates in solution.

Introduction and discussion

The question of whether or not triorganosilyl perchlorates, $R_3SiOClO_3$, undergo ionization in solvents such as dichloromethane or sulpholane is currently the most controversial issue in organosilicon chemistry. Lambert and his colleagues have concluded from their experiments that the perchlorates $R_3SiOClO_3$ formed in situ from the hydrides R_3SiH and Ph_3CClO_4 ionize to give silicenium ions in such solvents [1,2]. They maintain, for example, that $Me_3SiOClO_3$ and $Ph_3SiOClO_3$ are extensively ionized to free ions in sulpholane, and that the latter perchlorate is substantially ionized to give ion pairs in CH_2Cl_2 [3]. Olah and his colleagues have failed to detect any evidence for ionization, and attribute the effects observed by Lambert and his colleagues to formation of perchloric acid by the action of traces of water in the solvents [4].

The purpose of this note is point out that the protagonists in the controversy appear not to have taken account of a relevant item of information concerning organosilicon perchlorates, namely that the sterically hindered $TsiMe_2SiOClO_3$ ($Tsi = (Me_3Si)_3C$) undergoes solvolysis in methanol fairly slowly, with a half-life of ca. 24 min at 27.5 °C, and very slowly, if at all, in CF_3CH_2OH [5] *. If triorganosi-

---

* In the light of information available for other $TsiMe_2SiX$ and $t\text{-}Bu_3SiX$ compounds [6] it is very probable that $t\text{-}Bu_3SiOClO_3$, like $t\text{-}Bu_3SiOSO_2CF_3$, also reacts only slowly with methanol.

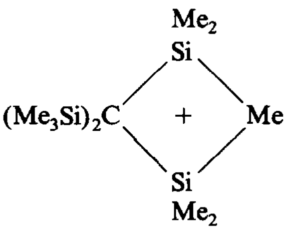
0022-328X/91/$03.50

lyl perchlorates were, indeed, ionized to a physically detectable extent in a solvent such as CH_2Cl_2, or even sulpholane, it seems very unlikely that $TsiMe_2SiOClO_3$ would not be significantly ionized in the powerful ionizing solvents MeOH and CF_3CH_2OH, and if it were then there would be immediate conversion into $TsiMe_2SiOMe$ or $TsiMe_2SiOCH_2CF_3$.

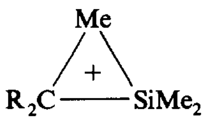
For Ph_3SiClO_3 to be ionized (to give an ion pair) in CH_2Cl_2 to the extent reported by Lambert and his colleagues [3] the rate of ionization would have to be comparable with that of the reverse reaction between Ph_3Si^+ and ClO_4^-, and if their data for ionization of $Me_3SiOClO_3$ in sulpholane [1] are correct then the ionization must be several times faster than the reaction between the ions even at low concentrations. Even if the rate of ionization of $TsiMe_2SiOClO_3$ in MeOH or CF_3CH_2OH were many orders of magnititude lower there would still be virtually instantaneous reaction with these solvents. For the solvents mentioned, Kosower's Z-values, which probably give the best guide to the general ionizing power of the solvents for present purposes, are: CH_2Cl_2 64.2, sulpholane 77.5, MeOH 83.6 [7]. As indicated by Winstein's Y-values [8] the weakly nucleophilic CF_3CH_2OH (Y, 1.80), in which no detectable solvolysis of $TsiMe_2SiOClO_3$ occurs, is a markedly better ionizing solvent than MeOH (Y, -0.92).

It might be argued that ionization of $TsiMe_2SiOClO_3$ is inhibited by steric hindrance to solvation of the silicenium ion $TsiMe_2Si^+$, but against this it must be noted that the ionization would be favoured by the release of steric strain, and crowding in alkyl halides enhances the ease of ionization [9]. In any case it is difficult to accept that the steric hindrance would reduce the overall solvation in MeOH or CF_3CH_2OH, in which solvation of the anion would be especially effective, substantially below that for Ph_3Si^+ and ClO_4^- in the weakly ionizing CH_2Cl_2 or even in sulpholane.

The actual mechanism of methanolysis of $TsiMe_2SiOClO_3$ is largely irrelevant to the main issue, that of the possible ionization of triorganosilyl perchlorates, except that if, as is now thought [10], the methanolysis does not involve a cationic intermediate at all (as was at one time thought it might [5,11]), then any ionization to give the silicenium ion $TsiMe_2Si^+$, or even the more stable bridged ion **1**, must be even slower than the observed rate of the methanolysis. The transient bridged cation **1**, is, however, generated by, for example, reaction of $TsiMe_2SiI$ with silver salts in CH_2Cl_2, MeOH, or CF_3CH_2OH, or with the powerfully electrophilic solvent CF_3CO_2H [12].



(1)



(2)

The view that significant ionization of triorganosilyl perchlorates in CH_2Cl_2 or sulpholane is very unlikely has no direct bearing on the question of whether or not there is evidence for the formation of silicenium ions as transient intermediates in solution in various substitutions and rearrangements, except in so far as acceptance of the conclusions reached by Lambert et al. has led several authors to propose such intermediates in cases in which it would previously have been usual to avoid them. However, some brief comments on this issue may be pertinent. Olah and his colleagues accept that such ions are involved as intermediates [4], and there is no reason to doubt that there will in time be clear demonstrations of their participation, but in only one of the papers to which Olah et al. make reference is the evidence at all compelling, namely that by Apeloig and Stanger concerned with a reaction in which a carbenium ion appears to rearrange to a silicenium ion [13]. The mechanism they propose, involving formation of a silicenium ion (within a solvent-separated ion-pair), when modified as suggested by Kevill [14], provides the simplest interpretation of the experimental observations, but the possibility cannot be ruled out that a methyl-bridged ion of type **2**, analogous to **1**, is formed instead of the simple silicenium ion, and is then attacked by the various nucleophiles at carbon or silicon [14].

The only other strong case for the intermediacy of silicenium ions in solution is that made by Chojnowski and his colleagues in respect of the reactions of organosilicon hydrides with trityl salts such as Ph_3CBF_4 in CH_2Cl_2 [15], but even here a serious difficulty arises. This is that, as Chojnowski et al. stated, for the formation of R_3Si^+ in a process not involving nucleophilic attack at silicon in the rate-determining step there should be a low sensitivity to steric effects, and they took the small variation in rate for the compounds R_3SiH with R = Me, Et, n-Pr, n-Bu, and n-hexyl as evidence for such a low sensitivity; however, they found the rate of reaction of $t\text{-}Bu_3SiH$ too low to measure, showing that the reaction is in fact markedly subject to steric hindrance. (It is also very significant that Chojnowski et al. found $(EtS)_3SiH$ to be much less reactive than Ph_3SiH and Me_3SiH whereas Lambert and his colleagues found $(EtS)_3SiOClO_3$ to be especially readily ionized [3]. The conclusions reached by the two groups cannot both be correct, and since the relevant transition state for the reaction with Ph_3CBF_4 evidently has much silicenium ion character, even though may not actually lead to a silicenium ion, further doubt is cast on the significance of the data reported by Lambert et al. [1–3]).

It is noteworthy that for the analogous reaction of R_3SiH compounds with $AgClO_4$ in toluene, in which the rate-determining step appears to involve abstraction of hydride by Ag^+, it was pointed out many years ago that the results, including the reduction in rate on going from $(C_6H_5CH_2)_3SiH$ to $(m\text{-}ClC_6H_4CH_2)_3SiH$ (a larger effect, even after allowance for the different number of benzyl groups, than that on going from $(C_6H_5CH_2)Me_2SiH$ to $(m\text{-}ClC_6H_4CH_2)\text{-}SiMe_2H$ in reaction with Ph_3CBF_4 [15], indicating greater development of positive charge on silicon in the former reaction) pointed towards generation of the ion R_3Si^+ [16,17]. However, the large effect of steric hindrance revealed by the very low reactivity of $i\text{-}Pr_3SiH$ was taken to imply that some nucleophilic participation by the perchlorate anion must be involved in the transition state, even if only in a very weak (but still essential) interaction very little removed from nucleophilic 'solvation' on the way to a covalent bond [17]. The existence of such weak nucleophilic participation by the anion in the case of the reaction with Ph_3CBF_4 and related salts would account for the large influence of steric hindrance in that reaction and the smallness of the effect of changing the anion within the narrow range used. If a convincing case can be made, in spite of the large steric effects, for the intermediacy of the ions R_3Si^+ in the reaction of R_3SiH compounds with Ph_3CBF_4 in CH_2Cl_2 then it would follow that the intermediacy of such ions in the reaction with $AgClO_4$ could also be accepted *.

It has long been recognized that, along with the absence of the resonance stabilization by substituents that is so important for carbenium ions, a major reason for the rarity of reactions in solution that can be shown to involve silicenium ion intermediates is that the great ease of nucleophilic attack at silicon favours mechanisms involving such attack [19]. When in the case of $TsiSiMe_2I$ the nucleophilic attack is greatly inhibited, a cation can be generated, rapidly in the reaction with silver salts and slowly in that with CF_3CO_2H, but it is the bridged species **1** not a simple silicenium ion [12]. The corresponding reactions are slower in the case of t-Bu_3SiI (which is comparable with $TsiSiMe_2I$ in reactivity towards nucleophiles [6]), and may proceed through t-Bu_3Si^+, though if a cation is formed it could possibly be a methyl-bridged species which is then nucleophilically attacked exclusively at silicon. It could be that in the reactions of R_3SiH compounds with Ph_3CBF_4 or $AgClO_4$, only in the case of sterically hindered hydrides such as t-Bu_3SiH is a silicenium ion generated.

Of course, as was pointed out some years ago, when starting from R_3SiX and R_3CX compounds in which X is halogen or an oxygen-centred ligand (but not H **) the greater strength of the Si–X than of the C–X bond will act to increase the energy required for the ionization of the Si–X relative to that of the C–X bond [21] (see also ref. 23), but this effect seems unlikely to prevent formation of ions from the silicon halides under the influence of powerful electrophiles such as silver salts or CF_3CO_2H. In view of information on the stabilities of silicenium ions in the gas phase derived experimentally and from calculations, it seems that in solution poor solvation of such ions relative to that of carbenium ions must be a major factor, and more important than initially suspected [19] ***. Since silicon is larger than carbon poorer solvation was to be expected [19] for non-specific electrostatic solvation (such as that in CH_2Cl_2; cf. ref. 23), but it is less likely for the specific nucleophilic type of solvation thought [24] to be important for carbenium ions in donor solvents such as MeOH; indeed, in view of the great affinity of silicon for nucleophiles, such solvation, though not the overall solvation, might even be expected to be more effective for silicenium than carbenium ions.

The discussion immediately above has an important bearing on the conclusions reached by Lambert and his colleagues. They find that $Me_3SiOClO_3$ is only a little less ionized than $Ph_3SiOClO_3$ in sulpholane and that $Ph_3SiOClO_3$ is extensively

---

* Marciniec, who also interpreted the results of a detailed study in terms of nucleophilic participation by the perchlorate ion, has shown that the effective electrophile is probably the ion pair dimer $(Ag^+ ClO_4^-)_2$ [18], but this does not affect the present argument.

** Wording used by Lambert and his colleagues appears, no doubt wrongly, to imply that they take this to mean that R_3Si^+ ions can be more readily produced in detectable concentrations by in situ treatment of R_3SiH with Ph_3CClO_4 than by starting from $R_3SiOClO_3$ [20].

*** However, if unbridged ions are involved in the rearrangement studied by Apeloig and Stanger then the energy of the solvated silicenium ion must be comparable with that of its solvated carbenium ion isomer (in which, though, nucleophilic solvation is inhibited). Furthermore, there is no difficulty in generating the transient bridged cation **1** in MeOH, CF_3CH_2OH, or CH_2Cl_2 [12] even though the charge is dispersed and, acccording to calculations [22], lies mainly on the Si atoms at the end of the bridge.

ionized in CH_2Cl_2, implying that $Me_3SiOClO_3$ should be significantly ionized in the latter solvent. Since the energy required to ionize $Me_3SiOClO_3$ can be confidently assumed to be substantially greater than that to ionize Me_3COClO_3, as is the case for ionization of the corresponding chlorides [23], and since the solvation of Me_3Si^+ is much less effective than that of Me_3C^+ in CH_2Cl_2 [23] (and probably also in sulpholane) then if the data reported by Lambert et al. are valid Me_3COClO_3 should be substantially ionized in CH_2Cl_2 and virtually completely so in sulpholane.

References

1 See J.B. Lambert and W. Schilf, J. Am. Chem. Soc., 110 (1988) 6364 and references therein.
2 J.B. Lambert and W.J. Schulz, Jr., in S. Patai and Z. Rappoport (Eds.), The Chemistry of Functional Groups. The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, Ch. 17.
3 J.B. Lambert, W.J. Schulz, Jr., J.A. McConnell and W. Schilf, J. Am. Chem. Soc., 110 (1988) 2201.
4 See G.A. Olah, L. Helliger, X.-Y. Li and G.K.S. Prakash, J. Am. Chem. Soc., 112 (1990) 5991.
5 C. Eaborn and F.M.S. Mahmoud, J. Chem. Soc., Perkin Trans. 2, (1981) 1309.
6 C. Eaborn and A.K. Saxena, J. Organomet. Chem., 271 (1984) 33.
7 E.M. Kosower, An Introduction to Physical Organic Chemistry, Wiley, New York, 1968, pp. 296–304.
8 J. March, Advanced Organic Chemistry, 3rd ed., Wiley, New York, 1985, p. 319; F.L. Schadt, T.W. Bentley and P.v.R. Schleyer, J. Am. Chem. Soc., 98 (1976) 7667.
9 J. March, Advanced Organic Chemistry, 3rd ed., Wiley, New York, 1985, p. 240.
10 D.B. Azarian, C. Eaborn and P.D. Lickiss, J. Organomet. Chem., 328 (1987) 255.
11 S.A.I. Al-Shali, C. Eaborn, F.A. Fattah and S.T. Najim, J. Chem. Soc., Chem. Commun., (1984) 318.
12 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organomet. Chem., 188 (1980) 179; C. Eaborn in H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Ellis Horwood, Chichester, 1985, pp. 123–130.
13 Y. Apeloig and A. Stanger, J. Am. Chem. Soc., 109 (1987) 272.
14 D.N. Kevill, J. Chem. Research, (S), (1987) 272.
15 J. Chojnowski, W. Fortuniak and W. Stańczyk, J. Am. Chem. Soc., 109 (1987) 7776.
16 C. Eaborn, J. Chem. Soc., (1955) 2517.
17 C. Eaborn, Organosilicon Compounds, Butterworth, 1960, pp. 208–209.
18 B. Marciniec, Z. Anorg. Allg. Chem., 495 (1982) 232.
19 C. Eaborn, Organosilicon Compounds, Butterworth, 1960, pp. 114–116.
20 J.B. Lambert and W.J. Schulz, Jr., in S. Patai and Z. Rappoport (Eds.), The Chemistry of Functional Groups. The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 1011; J.B. Lambert, W.J. Schulz, Jr., J.A. McConnell and W. Schilf, J. Am. Chem. Soc., 110 (1988) 2202.
21 L.H. Sommer, Stereochemistry, Mechanism, and Silicon, McGraw Hill, New York, 1965, p. 36.
22 A.J. Kos, personal communication, 1982.
23 S.K. Shin and J.L Beauchamp, J. Am. Chem. Soc., 111 (1989) 900.
24 D. Bethell and V. Gold, Carbonium Ions, Academic Press, 1967, pp. 139–144; T.W. Bentley and P.v.R. Schleyer, J. Am. Chem. Soc., 98 (1976) 7658; D.N. Kevill and S.W. Anderson, ibid., 110 (1986) 1579.