ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 604 (2000) 208–210

Journal of Organo metallic Chemistry

Carbanion mechanisms XXI. Solution acidity of triphenylsilane☆

Erwin Buncel *, T.K. Venkatachalam

Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

Received 4 February 2000; received in revised form 20 April 2000; accepted 24 April 2000

Abstract

Comparative acidity measurements have been performed between triphenylsilylpotassium and a series of arylmethanes by ^{1}H-NMR in tetrahydrofuran:

$Ph_3SiK + Ar_nCH_{4-n} \leftrightarrows Ph_3SiH + Ar_nCH_{3-n}K$

Metalation of the arylmethane was complete in the case of Ph_3CH (pK_a 31.4) and Ph_2CH_2 (pK_a 33.4) but with $(p\text{-}CH_3{\cdot}C_6H_4)_2CH_2$ (pK_a 35.1) ~50% metalation of the di-*p*-tolymethane occurred, indicating that the two acids have equal pK_a. No reaction occurred with $4\text{-}Ph{\cdot}C_6H_4{\cdot}CH_3$ (pK_a 38.7). Thus pK_a $Ph_3SiH \approx 35.1$ in THF. This represents the first solution measurement of the acidity of an organosilane. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silyl anions; Triphenylsilane; Acidity; pK_a in THF

---

1. Introduction

The concept of carbon acidity [1] is fundamental to a variety of structure-reactivity relationships in organic chemistry. It also has practical consequences as it reflects the stabilities of carbanions, key intermediates utilized in a multitude of synthetic transformations of organic molecules [2]. While much effort has been devoted in quantitating both thermodynamic [3] and kinetic [4] carbon acidities, relatively little is known about the acidities of hydrides of the other Group 14 elements, silicon, germanium, tin and lead. These elements have rich organic chemistry associated with them. For example, silyl anions are utilized in a variety of synthetic organic reactions [5]. Thus, knowledge of the acidities of organo silicon hydrides is of practical utility, as in the case of carbon acids.

Some studies of organosilane acidities have, in fact, been reported but these refer almost entirely to gas phase acidities [6]. Formation of silyl anions directly by deprotonation in an organic solvent has rarely been investigated though a number of organosilane derivatives are known to be deprotonated by potassium hydride [7]. It appeared to us that investigations of solution organosilane acidities, through deprotonation of the parent silanes, would be of value in allowing direct comparison with carbon acidity and extend the acidity scales established for carbon acids [1,3,4] to the other Group 14 elements. In continuation of our studies of carbanions [8] and of other Group 14 anions [9], we now present the results of what to our knowledge is the first determination of the solution acidity of an organosilane derivative relative to the corresponding carbon analogue.

2. Results and discussion

The classical method for determination of equilibrium carbon acidities [10] is via the reaction in Eq. (1):

$$R_1H + R_2M \leftrightarrows R_1M + R_2H \quad (1)$$

This has been used by Streitwieser to determine relative acidities in cyclohexylamine (CHA) [3a] and in tetrahydrofuran (THF) [3b], and by Bordwell in dimethyl sulfoxide (DMSO) [11]. The acid R_1H is al-

---

☆ For Part XX see Ref. [16].

* Corresponding author. Tel.: +1-613-5332653; fax: +1-613-5336669.

E-mail address: buncele@chem.queensu.ca (E. Buncel).

PII: S0022-328X(00)00242-4

lowed to equilibrate with R_2M, where M is an alkali metal; when R_1H is a much weaker acid than R_2H the position of the equilibrium is far to the left, and conversely the position is far to the right when the inverse acidity order obtains, but when they are comparable then the relative acidities are given directly by the ratio $[R_1H]/R_2H]$ which is determined usually by spectroscopic techniques such as NMR or UV–vis. We had previously used this method to evaluate by spectrophotometric techniques the equilibrium acidity of H_2 relative to a series of arylmethanes of known acidities in THF solvent [12], and similarly for NH_3 and CH_3NH_2 [13].

We have thus evaluated the acidity of triphenylsilane, Ph_3SiH, relative to the series of arylmethanes Ar_nCH_{4-n} ($n = 1–3$) of known pK_a values, in THF solvent, by means of the general reaction,

$$Ph_3SiK + Ar_nCH_{4-n} \rightleftarrows Ph_3SiH + Ar_nCH_{3-n}K \qquad (2)$$

starting with triphenylmethane, Ph_3CH, and going down the series of arylmethanes with decreasing acidities until equilibration would occur. Ph_3SiK was prepared by cleavage of $Ph_3SiSiPh_3$ with potassium metal in THF and was allowed to react with equimolar Ph_3CH. The position of equilibrium was monitored by ^1H-NMR; the ^1H-NMR characteristics of Ph_3SiK and Ph_3CK have been reported previously [14,15].

The results, given in Table 1, show that Ph_3SiH is a weaker acid than Ph_3CH (pK_a 31.4) since the metalation of the arylmethane proceded to completion. Similarly, it was found that Ph_3SiH is also a weaker acid than Ph_2CH_2 (pK_a 33.4). However, when the reaction was performed with di-*p*-tolymethane (pK_a 35.1) the metalation went half way to completion indicating that the two acids have equal pK_a. No reaction was observed in the case of *p*-phenyltoluene (pK_a 38.7). It is noted that these pK_a values refer to ion pair acidity, following Streitwieser [3a].

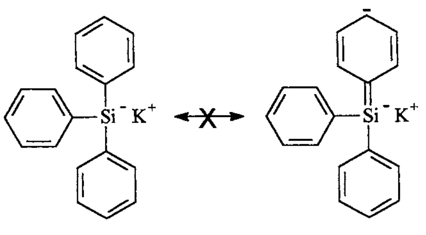
Table 1
Results on extent of metalation of arylmethanes in the equilibration with Ph_3SiK in THF solvent from ^1H-NMR experiments [a]

Reaction	Time	Temperature (°C)	Metalation (%) [b]
$Ph_3SiK + Ph_3CH$	30 min	−40	90
$Ph_3SiK + Ph_3CH$	45 min	−40	95
$Ph_3SiK + Ph_3CH$	24 h	25	95
$Ph_3SiK + Ph_2CH_2$	45 min	−40	10
$Ph_3SiK + Ph_2CH_2$	45 min	25	40
$Ph_3SiK + Ph_2CH_2$	24 h	25	95
$Ph_3SiK + (p\text{-}MeC_6H_4)_2CH_2$	45 min	−40	0
$Ph_3SiK + (p\text{-}MeC_6H_4)_2CH_2$	24 h	25	50
$Ph_3SiK + (p\text{-}MeC_6H_4)_2CH_2$	48 h	25	60
$Ph_3SiK + p\text{-}PhC_6H_4CH_3$	30 min	−40	0
$Ph_3SiK + p\text{-}PhC_6H_4CH_3$	45 min	−40	0
$Ph_3SiK + p\text{-}PhC_6H_4CH_3$	24 h	25	0

[a] Cyclohexane internal reference (δ1.43); 0.2 M Ph_3SiK and arylmethane; spectra taken on AM-400 Bruker spectrometer.

[b] Estimated from relative integrals of Si–H and ArC–H peaks with uncertainty of ±10%.

The finding that Ph_3SiH is a weaker acid than Ph_3CH is in accord with previous NMR [15] and UV–vis [16] evidence that charge delocalization over the phenyl groups in Ph_3Si^- does not occur to significant extent, i.e. structures such as **1b** contribute to negligible extent:



1a **1b**

The present result on comparison of the pK_a of Ph_3SiH (35.1) with that of Ph_3CH (31.4) represents the first quantitative measure of the effect of lack of resonance stabilisation in the Ph_3Si^- anion on a fundamental thermodynamic property [17]. We plan to extend the studies to other organosilanes as well as hydrides of the other Group 14 elements.

3. Experimental

Hexaphenyldisilane ($Ph_3SiSiPh_3$) was prepared by the reaction of Ph_3SiCl with sodium metal using a procedure modified from that of Gilman [18]. A 100 ml 3-necked flask fitted with a reflux condenser, drying tube and nitrogen inlet was charged with 30 ml dry xylene (distilled over Na wire), 5 g Ph_3SiCl, and 0.7 g finely cut sodium. The reaction mixture was refluxed for 3 h during which time a deep violet coloured solution formed. After 6 h additional refluxing the contents were allowed to cool and the white precipitate was filtered. Traces of unreacted sodium were allowed to react with 95% EtOH and the solution was re-filtered to remove more product. The precipitate was washed with 95% EtOH, then with Et_2O, recrystallized from xylene and dried in vacuo, yielding 2.1 g $Ph_3SiSiPh_3$, m.p. 358–360°C, lit. [18] 362°C.

Triphenylsilylpotassium was prepared by reaction of $Ph_3SiSiPh_3$ with potassium metal flakes under dry THF in an ultrasonic bath at 0°C under an argon atmosphere [15]. The solutions were kept in septum-sealed reaction flasks in the ultrasonic bath for 3–4 h for reaction to be completed. The solution of Ph_3SiK in THF (0.2 M) was transferred by means of a syringe into argon-flushed NMR tubes containing one equivalent of the arylmethane and dry cyclohexane as an internal standard. Spectra were taken intermittently on a Bruker AM-400 spectrometer starting at −40°C and allowing to warm up gradually to 25°C.

Acknowledgements

Support of this research by a grant from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References

[1] (a) R.P. Bell, The Proton in Chemistry, 2nd ed., Cornell University Press, Ithaca, NY, 1973. (b) J.R. Jones, The Ionization of Carbon Acids, Academic Press, London, 1973. (c) R. Stewart, The Proton: Applications to Organic Chemistry, Academic Press, Orlando, FL, 1985.

[2] (a) E. Buncel, Carbanions. Mechanistic and Isotopic Aspects, Elsevier, Amsterdam, 1975. (b) V.A. Snieckus (Ed.), Advances in Carbanion Chemistry, vol. 1, JAI Press, Greenwich, Connecticut, 1992; vol. 2, JAI Press, Greenwich, Connecticut, 1994. (c) J.C. Stowell, Carbanion Organic Synthesis, Wiley, NY, 1979.

[3] (a) A. Streitwieser, E. Juaristi, L.L. Nebenzahl, in: E. Buncel, T. Durst (Eds.), Comprehensive Carbanion Chemistry, Part A, Structure and Reactivity, Elsevier, Amsterdam, 1980. (b) L. Xie, A. Streitwieser, J. Org. Chem. 60 (1995) 1339.

[4] (a) J.P. Guthrie, J. Cossar, A. Klym, Can. J. Chem. 65 (1987) 2154. (b) D.J. Hupe, D. Wu, J. Am. Chem. Soc. 99 (1977) 7648. (c) F.G. Bordwell, T.A. Cripe, D.L. Hughes, in: J.M. Harris, S.P. McManus (Eds.), Nucleophilicity, Advances in Chemistry Series 215, American Chemical Society, Washington, DC, pp. 137–153. (d) C.F. Bernasconi, Adv. Phys. Org. Chem. 27 (1992) 119. (e) A.J. Kresge, M. Leibovitch, Can. J. Chem. 68 (1990) 1786. (f) A. Streitwieser, D.R. Taylor, J. Chem. Soc. Chem. Commun. (1970) 1248. (g) J.R. Jones, K.T. Walkin, J.P. Davey, E. Buncel, J. Phys. Chem. 93 (1989) 1362.

[5] (a) E.W. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981. (b)W.P. Weber, Silicon for Organic Synthesis, Springer-Verlag, New York, 1983. (c) S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Parts 1 and 2, Wiley, Chichester, 1989.

[6] (a) D.M. Wetzel, L.E. Salomon, S. Berger, J.I. Brauman, J. Am. Chem. Soc. 111 (1989) 3835. (b) E.A. Brinkman, S. Berger, J.I. Brauman, J. Am. Chem. Soc. 116 (1994) 8304. (c) C.F. Rodriquez, A.C. Hopknson, Can. J. Chem. 70 (1992) 2234. (d) R. Damrauer, S.R. Kass, C.H. DePuy, Organometallics 7 (1988) 637.

[7] R.J.P. Corriu, C. Guerin, J. Organomet. Chem. 197 (1980) C19.

[8] (a) U. Edlund, E. Buncel, Prog. Phys. Org. Chem. 19 (1993) 225. (b) E. Buncel, B.C. Menon, J. Am. Chem. Soc. 102 (1980) 3499.

[9] (a) E. Buncel, T.K. Venkatachalam, Heteroatom. Chem. 5 (1994) 201. (b) U. Edlund, T. Lejon T.K. Venkatachalam, E. Buncel, J. Am. Chem. Soc. 107 (1985) 6408. (c) E. Buncel, T.K. Venkatachalam, U. Edlund, J. Organometal. Chem. 437 (1992) 85.

[10] D.J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, 1965, and refs. therein.

[11] (a) F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456. (b) R.W. Taft, F.G. Bordwell, Acc. Chem. Res. 21 (1988) 463.

[12] E. Buncel, B.C. Menon, J. Am. Chem. Soc. 99 (1977) 4457.

[13] E. Buncel, B.C. Menon, J. Organomet. Chem. 141 (1977) 1.

[14] U. Edlund, T. Lejon, T.K. Venkatachalam, E. Buncel, J. Am. Chem. Soc. 107 (1985) 6408.

[15] E. Buncel, T.K. Venkatachalam, B. Eliasson, U. Edlund, J. Am. Chem. Soc. 107 (1985) 303.

[16] E. Buncel, R.D. Gordon, T.K. Venkatachalam, J. Organometal. Chem. 507 (1996) 81.

[17] This statement needs to be qualified in the sense that electronegativity differences (Si versus C) would be a contributing factor to the pK_a difference between Ph_3SiH and Ph_3CH, in addition to the resonance stabilisation factor. We thank a referee for pointing out this qualification.

[18] H. Gilman, T.C. Wu, J. Am. Chem. Soc. 75 (1953) 3762.