Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

A KINETIC EFFECT OF d_π–d_π INTERACTIONS IN POLYSILANES

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(Received February 19th, 1968)

The concept of p_π–d_π bonding pervades much of inorganic chemistry, but some of the consequences of d_π–d_π bonding have only recently been appreciated and given an experimental foundation. The simplest systems for study contain relatively low lying but empty *d* orbitals on contiguous atoms, such as are found in the polysilanes. The overlap of *d* orbitals in polysilane chains has been shown to occur in excited states; perhaps the most impressive example being the ESR spectrum of the one electron reduction product of dodecamethylcyclohexasilane[1].

The experimental observations of *d* orbital interactions led the present author to undertake a kinetic study of the rates of base-catalyzed hydrolysis of the Si–H bond in the polysilanes listed in Table 1. Monosilanes have been studied under these or very similar conditions by a number of workers[2–7]. The reaction clearly involves nucleophilic attack on silicon with the Si atom bearing appreciably more negative charge in the transition state than in the ground state, as indicated [5,6] by a ρ^* of 3.5. It was anticipated that the transition state for this reaction could be stabilized and a rate acce-

TABLE 1

NMR AND KINETIC DATA OF THE SILANES STUDIED

Silane	δ (ppm)[a]	k_{rel}[b]
Me_3SiH	4.0 (ref. 10)	[c]
$Me_3SiSiMe_2H$	3.8 (ref. 11)	1.0
$(Me_3Si)_2SiMeH$	3.0	0.083
$(Me_3Si)_3SiH$	2.3 (ref. 12)	1.4–2.2[d]

[a] Measurements not taken in a common solvent or extrapolated to infinite dilution. [b] Second-order rate constants measured at 25° in 94.6 vol.% ethanol/water with KOH as catalyst. [c] Rate of hydrolysis of trimethylsilane has not been measured by the present investigator, but has been determined at 0° in 93.7 wt.% ethanol/water by Steward and Pierce[5]. From measurements at two temperatures, the rate constant for pentamethyldisilane has been extrapolated to 0°. The extrapolated rate constant gives a k_{rel} (Me_3SiH/$Me_3SiSiMe_2H$) of 0.78. [d] Imprecise and probably quite inaccurate estimated rate. Cleavage of Si–Si bonds competes with simple hydrolysis.

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leration observed if the added negative charge on the Si atom under attack could be distributed to adjacent Si atoms through d_π–d_π bonding. The system chosen is a fundamental one, but rather complex, for at least two additional factors may have significant influence on the reaction rate. The polar effect of added trimethylsilyl groups will have a rate retarding effect. The increased shielding of the Si–H proton in the NMR (see Table 1) is an indication of this inductive effect. Further, steric effects of relatively bulky trimethylsilyl groups may play a major role in determination of the rate.

Reactions were carried out in a twin-limbed reaction vessel[8] to insure vigorous agitation. Kinetics were measured as pseudo-first-order rate constants, which have been converted to second-order rate constants in Table 1. Rate constants were also measured for triethylsilane and triisopropylsilane, and good agreement was found with literature values both at the same temperature and when extrapolated to different temperature by means of the Arrhenius relationship. Pentamethyldisilane gives good pseudo-first-order kinetics to better than 80% reaction and affords the calculated volume of hydrogen within 2%. With branched-chain polysilanes, silicon–silicon bond cleavage is a competing reaction and more than one mole of H_2 is evolved. A good kinetic plot to 60% reaction could be obtained with 2-hydroheptamethyltrisilane, but tris(trimethylsilyl)silane gave rapid cleavage under basic conditions.

It has been shown with monosilanes that basic hydrolysis of Si–H compounds follows the Taft equation for aliphatic reactions[9] with a ρ^* of 3.5[5,6] and that the reaction is approximately as susceptible to steric effects as the basic hydrolysis of organic esters (isopropyldimethylsilane shows a deviation from the Taft plot of −0.42 log unit)[6]. The Taft plot shown in Fig. 1 includes points for methyl-, ethyl- and *n*-propyl-substituted silanes from the work of Steward and Pierce[5] (unnamed points in the Figure) as well as points for isopropyl- and tert-butylsilanes from Sommer and coworkers[6]. The latter compounds serve to show the importance of steric hindrance in the reaction system. Although no quantitative data are available on which to base a

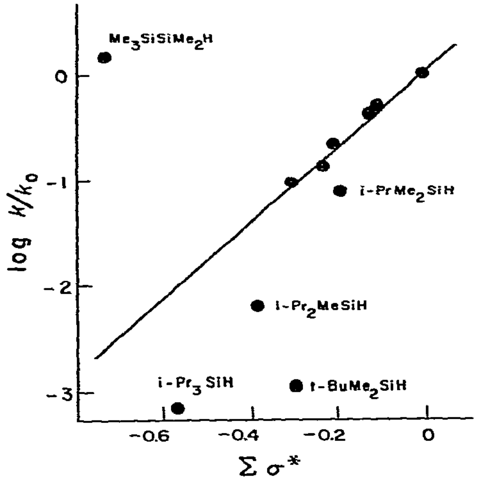

Fig. 1. Taft plot for the base-catalyzed hydrolysis of organosilanes. See text for identification of the sources of the kinetic data not obtained in the present studies.

judgement, it seems reasonable that a trimethylsilyl group would show a steric effect in this reaction comparable to that of an isopropyl group. The polar effect of a trimethylsilyl group may be predicted by means of the relationship: $\sigma^*(Me_3Si) = 2.8\ \sigma^*(Me_3SiCH_2) = -0.73$. Combining the expectations of polar and steric effects, one would anticipate a rate for pentamethyldisilane which would give a point somewhat below the line in the Taft plot. Instead, the point falls more than 2.5 log units above the line, indicating a rate factor of *ca.* 1000 due to an effect not taken into account. The plot in Fig. 1 has not been extended to include the trisilane, 2-hydroheptamethyltrisilane, which falls *ca.* 4 log units above the line.

The rather large rate accelerations observed in this work may be most reasonably attributed to *d* orbital overlap resulting in stabilization of the transition state for nucleophilic substitution. Similar effects should be widely observable in systems capable of d_π–d_π bonding, and some of these are being presently investigated.

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation through a postdoctoral fellowship. The author is grateful to Prof. C. Eaborn for stimulating discussions during the course of this work.

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