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# THE BASICITIES OF SOME ORGANOSILICON-, ORGANOGERMANIUM- AND ORGANOTIN-SUBSTITUTED PYRIDINES

D. G. ANDERSON, J. R. CHIPPERFIELD AND D. E. WEBSTER
*The University, Hull (Great Britain)*

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## SUMMARY

The $pK_a$ values have been measured of some organosilicon-, -germanium-, or -tin-substituted pyridines. For the compounds studied the $Me_3M$ group (M = Si, Ge, or Sn) in the 2-, 3-, or 4-position of pyridine is electron donating which is contrary to the observed effects of these groups when *p*-substituted in benzoic acids. The 2-substituted pyridines show exalted $pK_a$ values due to the formation of a complex with the solvent.

## INTRODUCTION

The $pK_a$ values of substituted benzoic acids and substituted pyridines have been used as measures of the electron donating or withdrawing abilities of substituent groups. The $pK_a$ values of benzoic acids substituted with an organosilicon, organogermanium, or organotin group have been measured by Chatt and Williams[1,2]. They found that the compounds *p*-$Me_3M$–$C_6H_4COOH$ (M = Si, Ge, or Sn), were all slightly stronger acids than benzoic acid, and suggested that, although the $Me_3M$– group donates electrons to the aromatic ring through a $\sigma$ bond, electrons are returned back to the silicon, germanium, or tin through a $p_\pi$–$d_\pi$ bond between the metal and the aromatic ring to an extent that outweighs the electron donation. They also found

TABLE 1

$pK_a$ VALUES OF SUBSTITUTED PYRIDINES ($RC_5H_4N$) AT 25°

| R | $pK_a$ | | |
|---|---|---|---|
| | 2-Subst. | 3-Subst. | 4-Subst. |
| H | 5.21[a] | 5.21[a] | 5.21[a] |
| Me | 5.94[a] | 5.65[a] | 6.03[a] |
| $Me_3C$ | 5.76[a] | 5.82[a] | 5.99[a] |
| $Me_3Si$ | 6.63 | 5.57 | 5.57 |
| $Me_3Ge$ | 6.64 | | |
| $Me_3Sn$ | 7.57 | | |
| $Ph_3Si$ | 5.45 | | 5.10 |
| $Et_3Si$ | 6.57 | | |

[a] From ref. 8.

that *p*-(triphenylsilyl)benzoic acid is a stronger acid than *p*-(trimethylsilyl)benzoic acid.

We have prepared some similarly substituted pyridines, and measured their basicities in aqueous methanol by potentiometric titration. The results are shown in Tables 1 and 2.

TABLE 2

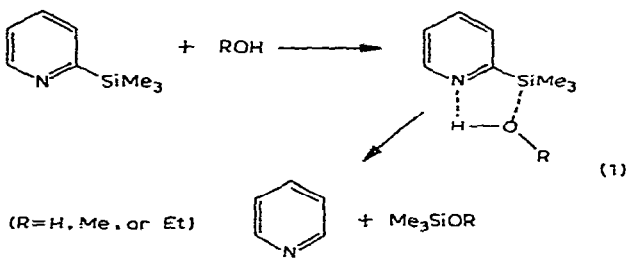
$pK_a$ VALUES OF DISUBSTITUTED PYRIDINES AT 25°

| | |
|---|---|
| 2,6-Dimethylpyridine (2,6-lutidine) | 6.69[a] |
| 2-(Trimethylsilyl)-4-methylpyridine | 7.51 |
| 2-(Trimethylsilyl)-6-methylpyridine | 7.58 |

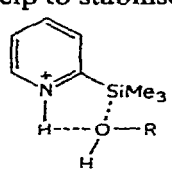
[a] From ref. 8.

## DISCUSSION

2- and 4-substituted pyridines usually have similar $pK_a$ values, for example, 2- and 4-methylpyridine (Table 1)*. In contrast 2-(trimethylsilyl)pyridine is a stronger base than 4-(trimethylsilyl)pyridine [the $pK_a$ value is 1.06 units greater (Table 1)], and 2-(triphenylsilyl)pyridine is a stronger base than 4-(triphenylsilyl)pyridine [the $pK_a$ value is 0.35 units greater (Table 1)]. This indicates that there is a specific effect associated with an organosilyl group at the 2- or the 4-position of a pyridine ring.




We have observed that 2-(trimethylsilyl)pyridine is solvolysed in methanol, in contrast to the 3- and 4-isomers which are not, and we have proposed the reaction mechanism given in eqn. 1, involving a cyclic activated complex (I)[4,5]. The corresponding cation could also form a cyclic complex (II) with methanol. The greater basicity of 2-(trimethylsilyl)pyridine requires the complex (II) to be more stable than a complex of the reactants similar to (I). On energetic grounds this would be expected as (II) contains an O–H hydrogen bond which would be expected to be stronger than the N–H hydrogen bond in (I). The positive charge on the nitrogen of (II) should also help to stabilise this complex. Furthermore, (II) would not be expected to break




II

* 4-tert-Butylpyridine is a stronger base than the 2-isomer (Table 1) because of steric effects[3].

down into the pyridinium ion and methoxytrimethylsilane as the proton which is being transferred from the solvent to the pyridine ring must first be coordinated to the nitrogen which, in the pyridinium ion, is already occupied.

As we observed, 2-(trimethylsilyl)pyridine, which can form a complex, has an abnormally high $pK_a$ value compared with 4-(trimethylsilyl)pyridine which cannot, and similarly for the (triphenylsilyl)pyridines. This high value for a 2-substituted pyridine is also obtained for 2-(triethylsilyl)pyridine.

All $pK_a$ measurements and the arguments based on them refer to aqueous methanol. For comparison with other substituted pyridines the results in the Tables have been corrected to the values expected to be obtained in water. $pK_a$'s measured in 10 or 20% aqueous methanol are the same after correction. There will be similar species to (I) and (II) in water as kinetic measurements we have made on 2-substituted pyridines show that the free pyridine is hydrolysed, but the pyridinium ion is not.

We have also measured the $pK_a$ values of 2-(trimethylsilyl)-4-methylpyridine and 2-(trimethylsilyl)-6-methylpyridine (Table 2). The values are those expected from additivity of the effects of substituent groups.

An increase in the electron donating ability of a substituent usually increases the $pK_a$ value of the substituted pyridine. Thus, in all the silicon-, germanium- and tin-substituted pyridines that we have studied, save 4-(triphenylsilyl)pyridine, there seems to be net donation from the metal to the pyridine ring, *i.e.*, in terms of Chatt and Williams's hypothesis[1,2], the electron donation through the $\sigma$-bond outweighs the electron return through the $p_\pi$–$d_\pi$ bond. This is the opposite of what Chatt and Williams found for *p*-substituted benzoic acids, and presumably stems from the greater reluctance of the pyridine ring to release electrons because of the greater electronegativity of nitrogen compared with carbon (plus the formation of cyclic complexes in the case of the 2-substituted pyridines). This view is supported by the fact that the order of the $pK_a$'s of the 2-$Me_3M$-substituted pyridines, *viz.*, Si ~ Ge < Sn, unlike the order Si ~ Ge ~ Sn observed by Chatt and Williams, is the same as that observed by Bott, Eaborn and Walton[6] for the acid cleavage of the carbon–tin bond in the compounds $Me_3M$–$CH_2C_6H_4SnEt_3$ in which the $Me_3M$– group is separated from the aromatic ring by a methylene group and therefore $p_\pi$–$d_\pi$ bonding must be absent.

## EXPERIMENTAL

The substituted pyridines were prepared by methods to be described elsewhere[5]. Liquid compounds were purified by preparative gas–liquid chromatography, and solids were recrystallised. The NMR and IR spectra of the compounds were consistent with their structures.

The basicities of the pyridines were measured in aqueous methanol at 25°. The pyridine ($10^{-5}$ mole) was titrated with 0.1 *N* hydrochloric acid which was added at a constant rate from an "Agla" 0.5 $cm^3$ micrometer syringe driven by a synchronous electric motor. The pH of the solution was measured continuously during the addition with a pH meter (E.I.L. model 23A) fitted with glass and calomel electrodes. The pH meter was standardised with oxalate buffers[7] in the solvent used in the titration. The pH of the solution at which there were equal concentrations of pyridine and pyridinium ions was found from the titration curve. The bases pyridine, 2-picoline, 2,6-lutidine and 2,4,6-collidine were titrated to check the method, and the results agreed with those in the literature[8] to 0.05 $pK$ units.

2-$R_3M$-substituted pyridines undergo solvolysis in methanol[4] so these were dissolved in excess hydrochloric acid (forming the pyridinium species which does not solvolyse) and titrated with sodium hydroxide. Free pyridine is only formed during the titration, and thus solvolysis is minimised. Calculations from the kinetic data obtained on the solvolysis of 2-substituted pyridines show that at the point of half neutralisation less than 1 % of the pyridine formed has been solvolysed, even for the most reactive tin substituted pyridines. This was confirmed here as the $pK_a$ value obtained for the tin compound (7.57) was greater than the mean of the $pK_a$ values of the hydrolysis products (pyridine 5.12 and $Me_3SnOH$ 6.56)[9].

The $pK_a$ values of acids and bases in non-aqueous and partly aqueous solvents are not the same as those in water. Differences in the $pK$ values of similar substances remain the same however. Thus the difference in $pK_a$ values of pyridine and 2-picoline is about 0.73 $pK$ units whether the titration is done in water or in aqueous methanol. All the $pK_a$ values listed in Tables 1 and 2 have been corrected to the value which would be obtained in water (in which most of the organometallic substituted pyridines studied are insoluble).

Determination of the $pK_a$ of an acid by the measurement of the pH of a solution at half-neutralisation is not as accurate as the methods of Kilpi[10] or Grunwald[11] but allows the $pK_a$'s of these unstable 2-$R_3M$-substituted pyridines to be readily obtained.

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