THE EFFECT OF SOLVATION BY ACETONE ON THE BASICITY OF SILYLALKYLAMINES

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The relative basicity of fifteen methylethoxysilylalkylamines of the type $(CH_3)_{3-m}(C_2H_5O)_m.$ $.Si(CH_2)_nNH_2$ in acetone has been studied by potentiometric titration. For $n > 1$ the basicity increases with increasing m, which is likely due to increasing electronic interaction of the oxygen of acetone with the silicon of silylalkylamines. The basicity of silylmethylamines ($n = 1$) changes nonsystematically, probably as a consequence of the competing action of opposite effects.

Structure effects on the basicity of silylalkylamines of the type $(CH_3)_{3-m}(C_2H_5O)_m.$ $.Si(CH_2)_nNH_2$ (for $m = 0-3$ and $n = 1-4$) were studied by us earlier[1] by means of IR frequency shift, $\Delta\nu(C—D)$, due to hydrogen bonding between the amine and deuteriochloroform. The basicity of the compounds with $n = 1-4: 1 < 2 > 3 > 4 =$ $=$ n-butylamine agrees well with the quantum chemical calculation of gas phase basicity of the compounds $H_3Si(CH_2)_nNH_2$ reported by us[2] for $n = 0-3$. In IR spectroscopic determination of the basicity of amines dilute solutions of the compound in nonpolar tetrachloromethane are used so that the effect of the solvent upon the basicity order of amines can be exluded[3,4]. With the aim to estimate the role of solvation of model compounds, in the present work the relative basicity of silylalkylamines of the above mentioned type has been determined by potentiometric titration in a polar solvent.

EXPERIMENTAL

Potentiometric Titration

Titrations of studied organosilicon amines, the preparation of which was reported elsewhere[1], were carried out with the aid of p-toluenesulphonic acid (crystalline water was removed *in vacuo* by heating the acid to 60°C for 70 h.) Acetone was chosen as the solvent of both the compounds to be titrated and the titrating agent. The solvent was purified by the procedure usual for titration in nonaqueous media[5] and contained 0·27% water. For comparative purposes, measurements

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[*] Part CLXVI in the series Organosilicon Compounds; Part CLXV: This Journal *44*, 1434 (1979).

with the use of acetone dried further over 4A molecular sieve and containing less than 0·003% water were made, too. The water content in acetone was checked by a modified Fisher titrating agent[6].

Indication glass electrode (Radiometer, Copenhagen) of the type G-202-C was immersed into anhydrous acetone for several days before use. The reference electrode was K-100 calomel electrode (the same producer) filled with saturated potassium chloride solution in methanol. The potential of the electrodes was measured by electron tube pH-meter of the type PHK-1 which was equipped with a frequency condenser (Mechanika, Prague), the reading accuracy being 0·5 mV. Prior to each measurement the instrument was at operation for several hours, in order to attain a constant temperature of all the circuits. The titrating agent, *c.* 0·22 N *p*-toluenesulphonic acid in anhydrous acetone, was added in 0·025 to 0·1 ml portions and the potential was read at the moment when it changed less than by 1 mV during 30 s. The initial amine concentration was $1 \, . \, 10^{-4}$ mol/l (20 ml of acetone). Titration was carried out at a temperature of 25 ± 0·1°C in an atmosphere of nitrogen by which gas the titration solution was also stirred. The half neutralization potential $E_{1/2}$ was determined graphically[7] from the dependence of potential (mV) on the amount of the consumed acid (ml).

Although equimolar amounts of titrated substances were used and solutions were maintained at constant temperature, the measured $E_{1/2}$ values were not perfectly reproducible. For that reason the differences between potentials of studied silylalkylsubstituted amines and the potential of diphenylguanidine (DPG) as a reference compound were tabelated; $\Delta E_{1/2} = E_{1/2}(\text{DPG}) - E_{1/2}(\text{amine})$. Measurements were made in alternating way by which the $\Delta E_{1/2}$ values were reproducible within ±4 mV. Tabelated $\Delta E_{1/2}$ values are the arithmetic mean of five measurements.

RESULTS AND DISCUSSION

The choice of the solvent and titrating agent was limited by the nature of organosilicon amines to be titrated. Frequently used glacial acetic acid was not suitable in this case because of the possibility of side reactions. For similar reasons also hydroxylic solvents have to be excluded (possible exchange of alkoxy groups). Similarly, benzene and ether turned out to be unsuitable, likely due to the high resistance of titrated solutions[8]. Hall discussed[9] the suitability of a series of solvents for potentiometric titration of amines and stated that benzene, dioxane and chloroform show small potential range. Also chlorobenzene is not recommended for titration of bases, the p*K* values of which exceed 10 in water[10-12]. Of the remaining and available solvents, we have chosen acetone, the potential range of which was sufficiently broad. This solvent was also used for diluting the titrating agent, *p*-toluenesulphonic acid.

Differences in the half neutralization potential, $\Delta E_{1/2}$, in acetone, of all the compounds studied are presented in Table I. It holds that the higher the $\Delta E_{1/2}$, the stronger the base. As it is evident from Fig. 1 which shows in addition to $\Delta E_{1/2}$ values also the earlier reported[1] $\Delta\nu$ values and the calculated enthalpies of protonation of amines[2], ΔH, the trend in the basicity of nitrogen atom located in different distances with respect to the silicon is the same.

TABLE I

Half Neutralization Potentials, $\Delta E_{1/2}$, of Aminoalkylsubstituted Silanes of the Type $(CH_3)_{3-m}.(C_2H_5O)_mSi(CH_2)_nNH_2$ in Acetone (water content 0·27%)

Compound	$\Delta E_{1/2}$, mV[a]
$(CH_3)_3SiCH_2NH_2$	—67[b]
$(CH_3)_2(C_2H_5O)SiCH_2NH_2$	—28[b]
$(CH_3)(C_2H_5O)_2SiCH_2NH_2$	—90[b]
$(C_2H_5O)_3SiCH_2NH_2$	—86[b]
$(CH_3)_3Si(CH_2)_2NH_2$	—51[b]
$(CH_3)(C_2H_5O)_2Si(CH_2)_2NH_2$	—40
$(C_2H_5O)_3Si(CH_2)_2NH_2$	—36
$(CH_3)_3Si(CH_2)_3NH_2$	—57[b]
$(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$	—48
$(CH_3)(C_2H_5O)_2Si(CH_2)_3NH_2$	—42
$(C_2H_5O)_3Si(CH_2)_3NH_2$	—27
$(CH_3)_3Si(CH_2)_4NH_2$	—52
$(CH_3)_2(C_2H_5O)Si(CH_2)_4NH_2$	—52
$(CH_3)(C_2H_5O)_2Si(CH_2)_4NH_2$	—51
$(C_2H_5O)_3Si(CH_2)_4NH_2$	—33
n-$C_4H_9NH_2$	—67

[a] Maximal deviation ±4 mV. [b] $\Delta E_{1/2}$ values determined with the use of acetone containing <0·003% water were higher by 20 ± 5 mV in all cases.

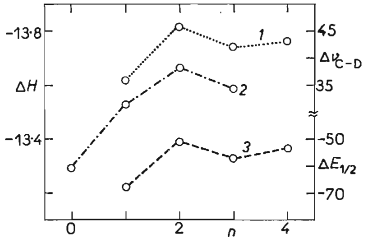

FIG. 1

Dependence of Calculated Enthalpies of Protonation of the Amines $H_3Si(CH_2)_nNH_2$ (ΔH in eV, *2*), Frequency Shifts $\Delta\nu$(C—D) (in cm^{-1}, *1*) and Half Neutralization Potentials ($\Delta E_{1/2}$ in mV, *3*) of the Amines $(CH_3)_3Si(CH_2)_nNH_2$ on n

The character of structural dependence of the basicity of silylalkylamines on the number of alkoxy groups in their molecule differs in the case of potentiometric titration in acetone somewhat from the spectroscopic[1] and quantum chemical[2] results. With silylalkylamines containing nitrogen in positions 2, 3 and 4 with respect to the silicon, the relative basicity, which increases with increasing number of ethoxy groups, is higher than that of the organic reference compound. In each of three series mentioned, this basicity tends to increase with increasing number of ethoxy groups bonded to silicon, in contradistinction to the results of spectroscopic determination in tetrachloromethane, which show that the basicity tends to decrease with the increasing substitution of the silicon by ethoxy groups (within experimental errors, however). The effect of substitution of the silicon by ethoxy groups manifests itself in the opposite way, compared to the trend expected on the basis of the $-I$ effect of these groups. This fact could be accounted for by the pronounced polarity of acetone. The electron rich carbonyl oxygen may act as electron donor in interaction with silicon. If such an interaction took place, its role were increased with increasing withdrawal of electrons from silicon, *i.e.* with increasing substitution of this atom by electronegative ethoxy groups.

The dependence of the basicity of silylmethylamines on substitution of silicon is at present difficult to explain. Nonsystematic changes of the basicity of these compounds could be probably attributed to the competing action of several opposite effects, *i.e.* to the $+I$ effect of the silyl group and solvation (coordination of acetone to silicon atom) by which the basicity of the nitrogen atom would be increased, and, on the other hand, by hyperconjugation effect and steric hindrance of the amino group by the bulky silylmethyl group, which would lead to decrease in the basicity.

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