BASICITY OF CARBONFUNCTIONAL ORGANOSILICON COMPOUNDS AND MECHANISM OF THE α EFFECT

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On the basis of decomposition of the protonation energy resulting from Longuet–Higgins theory of proton affinity, the significant stereospecific effect of silyl substituents that manifests itself in basicity trends in a series of carbonfunctional organosilicon compounds has been analysed.

The substituent effect of silyl groups in carbonfunctional organosilicon derivatives differs markedly from the effect of simple alkyls. This difference is clearly demonstrated *e.g.* by basicity trends in series of carbonfunctional alcohols[1] and amines[2] of the type $(CH_3)_3Si(CH_2)_nX$ *vs* $CH_3(CH_2)_nX$ ($X = NH_2, OH$; $n = 1-3$).

While in the case of carbon compounds, the basicity increases monotonously in both series with increasing n, in the series of silyl substituted alcohols one observes basicity decrease. The basicity sequence for amines is by far more complex and is characteristic of the action of the so called α effect.

The above mentioned dramatic difference in the substituent effect of silyl groups compared to alkyls has been, of course, the subject of theoretical quantum chemical study, the results of which comport with observed trends in basicity[3,4]. In these studies, the protonation energy ΔE, calculated as the difference between energies of protonated and unprotonated molecule, was taken as the measure of basicity. The proton affinity calculated in this way represents, however, the quantity which includes — in certain respect — the effect of a number of different factors.

The aim of this work was to analyse in terms of structural factors trends in protonation energies for the series of carbon and analogous silicon compounds of the type $H_3M(CH_2)_nX$ ($M = C, Si$; $n = 1, 2$; $X = NH_2, OH$) and contribute thus to the elucidation of mechanism of the α effect. The analysis is based on the decomposition of total protonation energy resulting from Longuet–Higgins theory of proton affinity[5].

RESULTS AND DISCUSSION

Procedure for decomposition of protonation energy is described in detail in our earlier work[6]. Therefore, we present here only basic ideas to the extent necessary for purposes of this study.

Protonation energies defined as the difference in the energies of protonated and unprotonated molecule represent the work needed to transfer the proton in electrical field of the attacked molecule from infinity to the distance r_0 that characterizes the length of newly formed bond in the protonated molecule (Eq. (*1*)).

$$\Delta E = \int_{\infty}^{r_0} \frac{\partial E}{\partial r} \, \mathrm{d}r \qquad (1)$$

To calculate this integral, one can take advantage of the fact that the resultant value of ΔE does not depend on the integration path used. The integration indicated by Eq. (*1*) can be then divided formally into two separate steps. In the first one, the vacant 1*s* orbital localised on a hypothetical particle having charge $\lambda = 0$ is transferred from infinity to the distance r_0. In the next step, this particle is being charged such that its charge changes continously within the interval 0–1. At the end of this charging process, we find thus situation in which proton H^+ is localised at the distance r_0 from the molecule. On the basis of the just described two-step integration, also the expression for protonation energy ΔE can be divided into two contributions (Eq. (*2*)).

$$\Delta E = \Delta\varepsilon + \Delta\eta \, . \qquad (2)$$

The first contribution describes hypothetical transfer of vacant 1*s* orbital. It corresponds to a certain correction on the extent of the basis. This correction thus reflects the fact that in common quantum chemical description, the extent of *A*0 basis is different for protonated and unprotonated molecule (usually by 1*s* orbital on proton).

The second contribution $\Delta\eta$ describes the charging process and accompanying reorganisation of electron distribution. Its magnitude is, of course, dependent on the magnitude of charge λ and Eq. (*2*) holds for $\Delta\eta$ corresponding to $\lambda = 1$.

Eq. (*2*) represents the basis for discussion of the effect of structural factors on proton affinity. It should be stressed that the idea of decomposition of protonation energy as such is not new and has been used *e.g.* by Morokuma[7]. However, one should be aware of the fact that any process which describes the total interaction energy in terms of additive contributions is always ladden with subjectivity arising from model concepts on which this decomposition is based.

From this standpoint, the method based on Longuet–Higgins theory of proton affinity[5] represents just another possible alternative to Morokuma's decomposition. The convenient feature of the proposed decomposition lies in the fact that correction $\Delta\varepsilon$ on the extent of the basis represents a roughly constant contribution which is nearly independent of the type of compound and of protonated atom (0 *vs* N in alcohols and amines). This shows that differences in proton affinities in the series of structurally similar compounds results from "intrinsic" factors that are described by the

second term of Eq. (2). For purposes of further detailed interpretation of structural effect it is useful to introduce in terms of Longuet-Higgins theory of the proton affinity potential $\Phi(\lambda)$ Eq. (3).

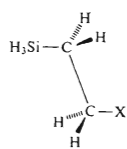
$$\Delta\eta(\lambda) = \lambda\,\Phi(\lambda) \tag{3a}$$

$$\Delta\eta(1) = \Phi(1) \tag{3b}$$

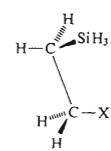
The expansion of this potential $\Phi(1)$ in the form of Taylor series (Eq. (4)) makes it possible to ascribe physical meaning to individual terms of this series. The first term of the right side of Eq. (4) expresses the electrostatic potential of static charge distribution of molecule A. The second and higher terms characterize distortion of this distribution that results from the appearance of charge λ in distance r_0. These terms thus express – to a certain degree – the polarizability of the molecule.

$$\Phi(1) = \Phi(0) + \left.\frac{\partial\Phi}{\partial\lambda}\right|_0 + \frac{1}{2}\left.\frac{\partial^2\Phi}{\partial\lambda^2}\right|_0 + \ldots \tag{4}$$

The present method of analysis of the protonation energy, based on the CNDO/2 approximation, was used to interpret basicity trends in the series of carbonfunctional alcohols and amines. Previous theoretical studies showed that CNDO/2 method describes correctly relative basicities in the series of these compounds as well as the stereoelectronic effect of silyl substituents[4]. These effects manifest themselves in that on going from α-functional derivatives H_3SiCH_2X to β-functional derivatives $H_3SiCH_2CH_2X$, that exist in energetically similar *anti* and *gauche* conformations (Scheme 1), one observes different trends in calculated ΔE values. Thus, while in anti



anti



gauche

SCHEME 1

conformation of molecular chain, the substituent SiH_3 causes basicity increase, in gauche conformation it decreases the basicity. At the same time, in analogous carbon series, the basicity increases monotonously irrespective of the conformation of alkyl group. CNDO/2 protonation energies as well as the value of their components are presented in Tables I and II.

TABLE I

Decomposition of protonation energy in the series of amines (all contributions in a.u.)

Compound	ΔE	$\Delta\varepsilon$	$\Delta\eta$	$\Phi(0)$
$H_3CCH_2NH_2$	−0·491	−0·383	−0·108	+0·049
$H_3CCH_2CH_2NH_2$[a]	−0·495	−0·383	−0·112	+0·048
$H_3CCH_2CH_2NH_2$[b]	−0·493	−0·384	−0·109	+0·049
$H_3SiCH_2NH_2$	−0·497	−0·385	−0·112	+0·049
$H_3SiCH_2CH_2NH_2$[a]	−0·502	−0·383	−0·119	+0·042
$H_3SiCH_2CH_2NH_2$[b]	−0·492	−0·388	−0·104	+0·058

Conformation [a] *anti*, [b] *gauche*.

TABLE II

Decomposition of protonation energy in the series of alcohols (all contributions in a.u.)

Compound	ΔE	$\Delta\varepsilon$	$\Delta\eta$	$\Phi(0)$
H_3CCH_2OH	−0·420	−0·385	−0·035	+0·101
$H_3CCH_2CH_2OH$[a]	−0·425	−0·385	−0·040	+0·098
$H_3CCH_2CH_2OH$[b]	−0·423	−0·386	−0·037	+0·102
H_3SiCH_2OH	−0·428	−0·387	−0·041	+0·100
$H_3SiCH_2CH_2OH$[a]	−0·435	−0·385	−0·050	+0·093
$H_3SiCH_2CH_2OH$[b]	−0·424	−0·391	−0·033	+0·110

Conformation [a] *anti*, [b] *gauche*.

TABLE III

Differences in proton affinity and its components in the series of α-carbonfunctional compounds H_3SiCH_2X with respect to the corresponding carbon derivatives

X	$\delta\,\Delta E$	$\delta\,\Delta\varepsilon$	$\delta\,\Delta\eta$	$\delta\,\Phi(0)$	δ (polarisability)
NH_2	−0·006	−0·002	−0·004	0·000	−0·004
OH	−0·008	−0·002	−0·006	−0·001	−0·005

Let us proceed now to detailed interpretation of the effect of structural factors. For this purpose, only relative changes in ΔE and their components in series of structurally similar compounds are decisive. Therefore, our discussion is based on comparison of the differences $\delta \Delta Q$ that are defined by Eq. (5) where Q stands for the corresponding molecular characteristics.

$$\delta \Delta Q_i = \Delta Q(\text{compound } i) - \Delta Q(\text{standard}) \qquad (5)$$

In order to evaluate the specific effect of silyl substituents in α-carbonfunctional derivatives, let us discuss the corresponding $\delta \Delta Q$ values in the series H_3SiCH_2X and CH_3CH_2X (standard). These data are given in Table III. It is seen that in both series of alcohols and amines, the difference in protonation energy is caused mainly by the difference in $\Delta\eta$, *i.e.* by intrinsic structural factors. Their more detailed analysis based on Eq. (6) (that was derived from Taylor series expansion (4)) shows that

$$\delta \Delta\eta = \delta \Phi(0) + \delta(\text{polarisability}) \qquad (6)$$

the substitution of carbon for silicon does not alter significantly the electrostatic potential $\Phi(0)$ in the vicinity of protonated centre. It implies that essentially the whole difference $\delta \Delta\eta$ can be ascribed to the second term of the equation, *i.e.* it is caused by the increased polarisability of silicon compared to carbon. Let us analyse in a similar way the pronounced stereospecific effect that reflects in the basicity of β-carbonfunctional alcohols and amines when going from anti to gauche conformers. Appropriate $\delta \Delta Q$ values are presented in Table IV, the standard being in this case the corresponding α-functional derivative H_3SiCH_2X. Table IV demonstrates that the

TABLE IV

Differences in proton affinity and its components in the series of β-functional compounds $H_3SiCH_2CH_2X$ with respect to α-functional derivatives H_3SiCH_2X as standards

X	$\delta \Delta E$	$\delta \Delta\varepsilon$	$\delta \Delta\eta$	$\delta \Phi(0)$	δ (polarisability)
NH_2	−0·005[a]	+0·002	−0·007	−0·007	0·000
	+0·005[b]	−0·003	+0·008	+0·009	−0·001
OH	−0·007[a]	+0·002	−0·009	−0·007	−0·002
	+0·004[b]	−0·004	+0·008	+0·010	−0·002

[a] *Anti* conformation of molecular chain, [b] *gauche* conformation of molecular chain.

difference in protonation energies is caused again mainly by intrinsic structural factors. These are represented by $\delta \Delta\eta$ quantities and not by correction on the magnitude of the $\delta \Delta\varepsilon$ basis.

Further detailed decomposition of $\delta \Delta\eta$ according to Eq. (6) is of interest. This decomposition shows that the pronounced stereospecific effect of silyl substituents results from differences in electrostatic potential $\Phi(0)$ between *gauche* and *anti* conformers. This demonstrates that the α effect is probably static one, since its manifestations are connected with differences in charge distribution in isolated molecules and are not thus the consequence of secondary structural changes induced by the protonation.

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