

## BASICITIES OF (HALOGENOALKYL)SUBSTITUTED SILICON COMPOUNDS. A QUANTUM CHEMICAL STUDY\*

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Received March 18th, 1976

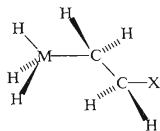
Enthalpies of protonation equilibria,  $\Delta H$ , of the compounds  $H_3M(CH_2)_nX$  ( $M = C, Si; X = F, Cl; n = 1-3$ ) were calculated for partially optimized geometries by CNDO/2 method neglecting silicon  $d$ -orbitals. The calculated values of  $\Delta H$  exhibit the same trends as the experimentally determined basicities and they are considerably affected by the conformation of the molecule.

In our previous work<sup>1</sup>, the basicities of organosilicon amines and alcohols of the type  $H_3Si(CH_2)_nX$  ( $X = NH_2, OH; n = 0-3$ ) were studied in relation to the mechanism of the  $\alpha$ -effect and to the problem of silicon  $d$ -orbital participation. The relative basicity of these compounds was measured by IR frequency shifts  $\Delta\nu_{OH}$  or  $\Delta\nu_{CD}$  observed in the formation of hydrogen bonds with phenol or deuteriochloroform employed as proton donors<sup>2,3</sup>. Since such measurements were carried out in very diluted solutions in non-polar solvent ( $CCl_4$ ), one can expect the order of  $\Delta\nu$  values to be comparable with the order of basicities measured in the gas phase. More recent experimental values  $\Delta\nu_{OH}$  of organosilicon halogeno derivatives of the type  $(CH_3)_3Si(CH_2)_nX$  ( $X = F, Cl; n = 1-3$ ) (ref.<sup>4</sup>) make an extension of our basicity studies to this series of compounds possible.

### CALCULATIONS

The CNDO/2 calculations were carried out for idealized tetrahedral geometries without the inclusion of silicon  $d$ -orbitals. For economical reasons the enthalpies  $\Delta H$  were calculated for silyl derivatives instead for trimethylsilyl derivatives. The Si—X bond lengths were taken from ref.<sup>5</sup> and all the other interatomic distances from the work<sup>6</sup>, except for the H—F and H—Cl bond lengths which were taken to be 0.96 and 1.27 Å, resp.<sup>7</sup> The geometry of  $\beta$ -functional derivatives was partially optimized with the respect to the rotation around the C—C bond. According to the CNDO/2 calculations the conformations with *anti*-periplanar arrangement of M—C and C—X bonds is the most stable one for the compounds of the type  $H_3M(CH_2)_2X$  ( $X = F, Cl; M = Si, C$ ).

\* Part CLI in the series Organosilicon Compounds; Part CL: This Journal 12, 1540 (1977).



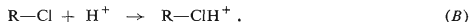
SCHEME 1

In  $\gamma$ -functional derivatives *anti*-conformation of the C—C—C—X chain was preserved and the  $H_3M$  group was placed into the energetically most favourable staggered conformation. In some cases the optimum conformations calculated by the CNDO/2 method differ from those obtained by the *ab initio* method<sup>8</sup> according to which the *syn*-clinal arrangement of C—C and C—F bonds is the most favourable in propyl fluoride. In regard to this finding, the protonation enthalpies  $\Delta H$  were calculated for both conformations and the results compared with the experimental data.

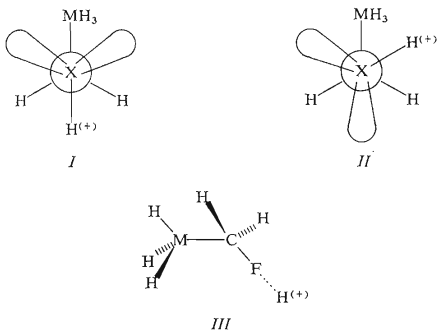
Reaction enthalpies,  $\Delta H$ , were calculated for the following reactions:



and



These reactions characterize the basicity of the compounds in the gas phase. There are three modes of protonation of the molecular active center (Scheme 2). The most favourable is the protonation mode *I*.



SCHEME 2

The results of the calculations are given in Tables I—III.

TABLE I  
Calculated Total Energies  $E$  (eV) and Reaction Enthalpies  $\Delta H$  (eV) for Reaction (A)

Compound	$E(\text{RX})$	$E(\text{RXH}^+)$	$\Delta H$
$\text{C}_2\text{H}_5\text{F}$	-1 245·940	-1 255·359	-9·419
$\text{C}_3\text{H}_7\text{F}^a$	-1 482·500	-1 492·094	-9·594
$\text{C}_4\text{H}_9\text{F}^a$	-1 718·942	-1 728·616	-9·675
$\text{H}_3\text{SiCH}_2\text{F}$	-1 151·943	-1 161·775	-9·832
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{F}^a$	-1 388·703	-1 398·593	-9·889
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{F}^a$	-1 625·191	-1 634·974	-9·783
$\text{C}_3\text{H}_7\text{F}^b$	-1 482·426	-1 491·916	-9·491
$\text{C}_4\text{H}_9\text{F}^b$	-1 718·845	-1 728·400	-9·555
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{F}^b$	-1 388·686	-1 398·307	-9·622
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{F}^b$	-1 625·115	-1 634·772	-9·657

<sup>a</sup> In *anti*-periplanar conformation. <sup>b</sup> In *syn*-clinal conformation.

TABLE II  
Calculated Total Energies  $E$  (eV) and Reaction Enthalpies  $\Delta H$  (eV) for Reaction (B) without Inclusion of Silicon and Chlorine  $d$ -Orbitals

Compound	$E(\text{RX})$	$E(\text{RXH}^+)$	$\Delta H$
$\text{C}_2\text{H}_5\text{Cl}$	- 928·020	- 936·060	-8·040
$\text{C}_3\text{H}_7\text{Cl}^a$	-1 164·572	-1 172·796	-8·224
$\text{C}_4\text{H}_9\text{Cl}^a$	-1 401·018	-1 409·324	-8·306
$\text{H}_3\text{SiCH}_2\text{Cl}$	- 834·167	- 842·496	-8·329
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{Cl}^a$	-1 070·922	-1 079·494	-8·573
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{Cl}^a$	-1 307·270	-1 315·686	-8·415
$\text{C}_3\text{H}_7\text{Cl}^b$	-1 164·462	-1 172·566	-8·104
$\text{C}_4\text{H}_9\text{Cl}^b$	-1 400·880	-1 409·042	-8·162
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{Cl}^b$	-1 070·741	-1 078·976	-8·234
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{Cl}^b$	-1 307·152	-1 315·404	-8·252

<sup>a</sup> In *anti*-periplanar conformation. <sup>b</sup> In *syn*-clinal conformation.

TABLE III

Calculated Total Energies  $E$  (eV) and Reaction Enthalpies  $\Delta H$  (eV) for Reaction (B) with Inclusion of Chlorine  $d$ -Orbitals (*anti*-periplanar conformation)

Compound	$E(\text{RX})$	$E(\text{RXH}^+)$	$\Delta H$
$\text{C}_2\text{H}_5\text{Cl}$	- 931.044	- 940.270	-9.226
$\text{C}_3\text{H}_7\text{Cl}$	-1 167.589	-1 177.027	-9.438
$\text{C}_4\text{H}_9\text{Cl}$	-1 404.036	-1 413.571	-9.535
$\text{H}_3\text{SiCH}_2\text{Cl}$	- 837.506	- 847.299	-9.793
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{Cl}$	-1 073.918	-1 083.741	-9.823
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{Cl}$	-1 310.288	-1 319.957	-9.669

## DISCUSSION

It is known that the CNDO/2 method correctly reproduces the basicities of alkyl alcohols and amines in the gas phase.

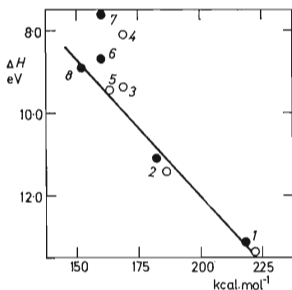


FIG. 1

Dependence of Calculated Protonation Enthalpies  $\Delta H$  on Experimental Values of Proton Affinities (gas phase in  $\text{CH}_3\text{X}$  and  $\text{C}_2\text{H}_5\text{X}$  Compounds

1 X =  $\text{NH}_2$ ; 2 X = OH; 3, 6 X = Cl with the inclusion of  $d$ -orbitals; 4, 7 X = Cl without the inclusion of  $d$ -orbitals; 5, 8 X = F). All the values of  $\Delta H$  are negative.

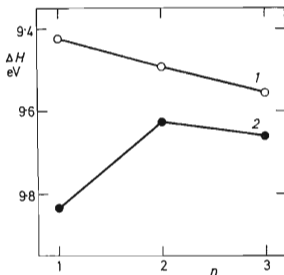


FIG. 2

Dependence of Calculated Protonation Enthalpies  $\Delta H$  on  $n$  in  $\text{H}_3\text{M}(\text{CH}_2)_n\text{F}$

1 M = C; 2 M = Si; *anti*-periplanar conformation of the chain. All the values of  $\Delta H$  are negative.

The dependence of the calculated  $\Delta H$  values on the protonaffinity<sup>9,10</sup> values is illustrated for methyl and ethyl alcohols, amines, and halogenoderivatives on Fig. 1. The fluoro derivatives fit the expected linear dependence equally well as the alcohols and amines. In the case of chloro derivatives larger deviations are observed. The agreement with the experimental results is better if the *d*-orbitals of chlorine are considered. One can, therefore, expect that the inclusion of the chlorine *d*-orbitals would allow a better description of the basicities even in the series of organosilicon derivatives  $H_3Si(CH_2)_nCl$ .

It is clear from Figs 2–6 that the calculated  $\Delta H$  values of carbonfunctional organosilicon halogeno derivatives strongly depend on the conformation of the molecule. Only in *anti*-periplanar conformation of Si—C and C—X bonds the trend in  $\Delta H$  values parallels that in  $\Delta\nu_{OH}$  values, and that even without the inclusion of the silicon *d*-orbitals. In *syn*-clinal conformations of these compounds the basicities of the  $\beta$ -functional derivatives are considerably lowered and, in the consequence, the order of basicities in isostructural series with the variable *n* is altered. Variation in the order of the calculated  $\Delta H$  values with the changes in the conformation were already noted in the study of the basicity of organosilicon amines and alcohols. Fluoro derivatives of organosilicon compounds in which, similarly as in amines, the *anti*-

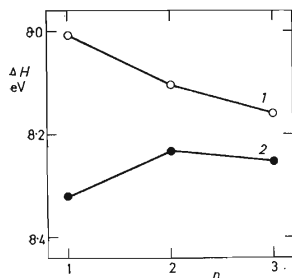


FIG. 3

Dependence of Calculated Protonation Enthalpies  $\Delta H$  on *n* in  $H_3M(CH_2)_nF$   
 1 M = C; 2 M = Si; *syn*-clinal conformation of the chain. All the values of  $\Delta H$  are negative.

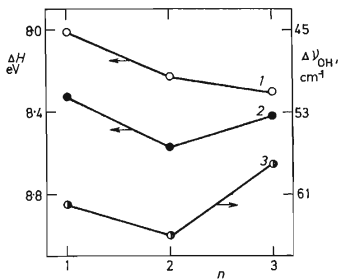


FIG. 4

Dependences of Protonation Enthalpies  $\Delta H$  Calculated for  $H_3M(CH_2)_nCl$  Compounds and of Experimental Values of  $\Delta\nu_{OH}$  (curve 3) in  $(CH_3)_3Si(CH_2)_nCl$  Compounds on the Number *n*

1 M = C, 2 M = Si; *anti*-periplanar conformation *n* of the chain; *d*-orbitals neglected. All the values of  $\Delta H$  are negative.

-periplanar conformation of Si—C and C—X bonds is preferred according to the CNDO/2 calculations, exhibit the same trend of the basicities. Organosilicon alcohols in which *syn*-clinal conformation is preferred, show, in an agreement with the experimental results<sup>2</sup>, a monotoneous decrease in the basicity when going from the  $\alpha$  to the to the  $\gamma$  derivative.

The trend in the calculated basicities of organosilicon chloro derivatives agrees with that found experimentally ( $\alpha < \gamma$ ) only if the chlorine *d*-orbitals are included. If only *s* and *p* orbitals are considered the basicity of the  $\beta$ -functional derivative is correctly calculated as the largest but the order of basicities of  $\alpha$  and  $\gamma$  functional derivatives is described incorrectly. The trends in the basicities of carbon derivatives are not sensitive to conformational changes.

The above facts obviously demonstrate that the variations in basicities of carbon-functional organosilicon derivatives are due to intramolecular interactions of a different type than those occurring in the series of carbon analogues. Detailed elucidation of such interactions would require much deeper analysis of orbital interactions. Such calculations are now in preparation in our laboratory.

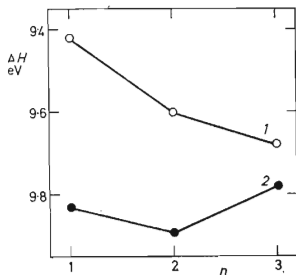


FIG. 5

Dependence of Calculated Protonation Enthalpies  $\Delta H$  on Number  $n$  in Compounds  $H_3M(CH_2)_nCl$

1 M = C, 2 M = Si; *syn*-clinal conformation of the chain; *d*-orbitals neglected. All the values of  $\Delta H$  are negative.

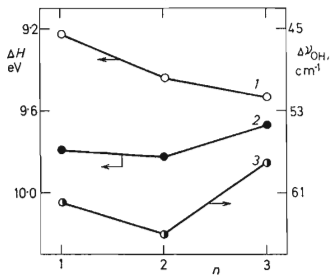


FIG. 6

Dependences of Protonation Enthalpies  $\Delta H$  Calculated for  $H_3M(CH_2)_nCl$  Compounds and of Experimental Values of  $\Delta\nu_{OH}$  in  $(CH_3)_3Si(CH_2)_nCl$  Compounds (curve 3) on Number  $n$

1 M = C, 2 M = Si; *anti*-periplanar conformation of the chain, chlorine *d*-orbitals included. All the values of  $\Delta H$  are negative.

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Translated by J. Schraml.