

## INFLUENCE OF SOLVENTS ON ELECTROCHEMICAL REDUCTION POTENTIALS OF CHLOROSILANES

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The reduction potentials of 1,1-dichloro- and 1-chloro-1-methylsilacyclobutane and their acyclic analogues were measured by cyclic voltammetry in the medium of anisole and dimethylformamide. The obtained values which reflect the simultaneous effect of angular strain and possible interactions of the depolarizer with the solvent were correlated with the results of quantum chemical calculations.

Electrochemical reduction of organosilicon halides in nonaqueous media has been studied much less thoroughly than the analogous reduction of carbon-halogen bond<sup>1</sup>. The works published hitherto deal with the electroreduction of phenylhalogen silanes<sup>2-9</sup> and simple alkylhalogensilanes of the type  $(\text{CH}_3)_{4-n}\text{SiCl}_n$  ( $n = 1-3$ )<sup>2,5, 10-12</sup> but no electrochemical studies of silacycles have been reported so far. From the point of view of electrochemical reduction, especially small cycles are interesting since the ease of their reduction can be influenced by a specific structural factor, the angular strain. The derivatives of silacyclobutane are attractive from both the physicochemical and synthetic point of view since many of them are precursors of silaethene derivatives<sup>13</sup>.

*Angular strain* in silacyclobutane derivatives manifested by the increased sensitivity of the Si—C bond toward splitting influences also other physicochemical properties. For example, the first ionization potential of 1,1-dimethylsilacyclobutane is by 1 eV lower than for analogous tetramethylsilane<sup>14,15</sup> indicating thus the increased energy of the highest occupied molecular orbital in the cyclic compound. Similarly, the UV spectra of silacyclobutanes show a considerable bathochromic shift of the long-wave band<sup>16</sup>, which can be attributed to a decrease of the difference between the energetic levels of frontier orbitals (HOMO–LUMO). On the basis of UV measurements only it is not, however, possible to decide whether this decrease is exclusively due to increased energy of HOMO or whether this effect is combined with a decrease of the LUMO energy. This problem can be resolved experimentally by measurements of electrochemical reduction potentials. The philosophy underlying the use of this technique is based on the simple model describing the formation of the radical anion

which is the primary intermediate of the electrochemical reduction as a process in which an electron enters into the lowest unoccupied molecular orbital (LUMO)<sup>17</sup>.

Since the LUMO energies are easily accessible by quantum chemical calculations, a comparison with the experimental values of reduction potentials enables one to discuss, in a series of structurally related compounds, the influence of structural factors on electrochemical reduction.

In view of the fact that the measurements were carried out in nonpolar anisole and in dipolar aprotic dimethylformamide (DMF) and the results in both solvents dramatically differ, we attempted to include in quantum chemical calculations the effect of the polarity of the medium. For this purpose the so-called solvation model proposed by Klopman<sup>18</sup> and modified to the level of CNDO approximation by Miertuš<sup>19</sup> was adopted. Of all solvation interactions this simple model describes only the part corresponding to the electrostatic effect of the polar medium and does not involve specific interactions such as *e.g.* the formation of donor-acceptor complexes between the solvent and depolarizer. Despite of this shortcoming this simplified model may substantially contribute to the elucidation of the mechanism of electrochemical reduction. Its use is based on the following simple idea. The calculations lead to LUMO values which reflect either purely structural effects (if  $\epsilon = 1$ ) or are corrected for electrostatic effects of the polar medium (if  $\epsilon > 1$ ). By comparing the calculated values of LUMO energies for the cases  $\epsilon = 1$  and  $\epsilon > 1$  with the experimental values of the reduction potentials it is possible to separate to some extent the effect of angular strain from nonspecific and specific solvation interaction effects of the reaction medium.

## EXPERIMENTAL

Dimethylformamide (Lachema, Brno) was dried for several days over anhydrous copper sulphate. Before use it was rectified *in vacuo* and further dried by activated neutral alumina<sup>20</sup>. Anisole (Lachema, Brno) was dried before use by boiling with sodium and rectified in argon atmosphere. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) (Fluka, Switzerland) were recrystallized from water and dried at 60°C *in vacuo*. 1,1-Dichlorosilacyclobutane and 1-chloro-1-methylsilacyclobutane were prepared by the published methods<sup>21</sup>. All organosilicon halides were rectified in argon atmosphere before use.

Cyclic voltammetric curves were recorded on PAR-175 type apparatus. Measurements were carried out at the laboratory temperature in argon atmosphere. Platinum microelectrodes were employed as working and auxiliary electrodes. For measurements in the medium of anisole, an Ag/AgNO<sub>3</sub> reference electrode was used, the potential of which was +0.63 V against saturated calomel electrode (s.c.e.)<sup>22</sup>. For measurements in DMF a Cd/CdCl<sub>2</sub> reference electrode was used with the potential -0.75 V against s.c.e.<sup>23</sup>. The reduction potentials are given in Table I.

## THEORETICAL

Quantum chemical calculations for the studied series of compounds were performed

by the semiempirical CNDO/2 method<sup>24</sup>. The influence of the polarity of the medium on the values of LUMO energies was included by the so-called solvaton model<sup>18,19</sup>. The geometry of all alkylchlorosilanes was derived from idealised tetrahedral arrangements with standard bond lengths<sup>24,25</sup> ( $r_{C-H} = 0.109$  nm,  $r_{Si-C} = 0.187$  nm,  $r_{Si-Cl} = 0.205$  nm). The geometric parameters for both silacyclobutane derivatives were derived from experimentally found bond lengths, dihedral and valence angles<sup>26-29</sup>. The possible distortion of the molecular geometry by the influence of the polar medium was not taken into consideration and the calculations were carried out with the same geometry for all values of dielectric constant  $\epsilon$ .

The calculated values of LUMO energies for the compounds under study are given in Table II. The values for  $\epsilon = 2$  (in anisole) do not differ too much from those for  $\epsilon = 1$  (approximation of isolated molecule) and only for  $\epsilon = 37$  the values are shifted more significantly suggesting the role of the solvent effect.

TABLE I

Reduction potentials  $E_p$  (against s.c.e.) for chloro derivatives of silacyclobutane and its acyclic analogues obtained by cyclic voltammetry in anisole and DMF

Compound	$E_p(V)^a$	$E_p(V)^b$
$(CH_2)_3SiCH_3Cl$	-0.58	-1.62
$(CH_2)_3SiCl_2$	-0.51	-1.11
$(CH_3)_3SiCl$	-1.11	-0.50
$(CH_3)_2SiCl_2$	-0.93	-0.60

<sup>a</sup> Anisole,  $0.2 \text{ mol l}^{-1}$  TBAP,  $2 \text{ mmol l}^{-1}$  depolarizer concentration; <sup>b</sup> DMF,  $0.1 \text{ mol l}^{-1}$  TEAP,  $1.5 \text{ mmol l}^{-1}$  depolarizer concentration.

TABLE II

Calculated LUMO energies (in atomic units, a.u. = 2622.8 kJ/mol) for the studied chlorosilacyclobutanes series and their acyclic analogues and for different values of dielectric constant  $\epsilon$

Compound	$\epsilon = 1$	$\epsilon = 2$	$\epsilon = 37$
$(CH_2)_3SiCH_3Cl$	0.065	0.068	0.075
$(CH_2)_3SiCl_2$	0.035	0.037	0.043
$(CH_3)_3SiCl$	0.072	0.074	0.077
$(CH_3)_2SiCl_2$	0.048	0.051	0.057

## RESULTS AND DISCUSSION

The pronounced effect of the solvent on reduction potentials was demonstrated on the example of anisole and DMF as solvents which differ by the polarity, content of traces of water and ability to form donor-acceptor complexes with halogensilanes<sup>30-32</sup>. In the previous study<sup>12</sup> it was shown that owing to its low polarity and low ability to enter into specific interactions with depolarizer anisole behaves as an "inert" solvent for the electrochemical measurements. The reduction potential measured in this solvent can be thus regarded as reflecting purely structural effects undistorted by the solvent effect<sup>12</sup>. In the case of 1-chloro substituted silacyclobutanes in anisole, the data from Table I reveal the easier reduction than in the case of acyclic analogues. In the light of the above considerations it is apparent that this better reducibility can be attributed to the increase of the angular strain in cyclic compounds. This conclusion is supported also by the calculated values of LUMO energies for anisole (Table II,  $\epsilon = 2$ ).

Another structural effect manifesting itself in the series of the studied compounds is represented by the increase in reducibility with increasing number of Cl atoms. This phenomenon, which is again in accord with the calculated values of LUMO energies, is entirely analogous to the trends observed in other series as *e.g.* alkylhalides<sup>33</sup> and halides of organometallic compounds of the type  $(\text{CH}_3)_{4-n}\text{MCl}_n$  ( $n = 1-3$ ,  $\text{M} = \text{Si, Ge, Sn}$ )<sup>34</sup>.

In the case of DMF the situation is much more complicated. In addition to possible solvolysis of Si-Cl bonds due to the effect of traces of residual water, the main complicating factor is represented by the possible formation of complexes of this solvent with halogensilanes<sup>30-32</sup>. Hence the values of reduction potential  $E_p$  in the medium of DMF will not probably reflect purely structural effects but they can be distorted by the contaminating influence of both specific and nonspecific interactions between the depolarizer and DMF.

The influence of possible complexation on the reduction potentials of halogensilanes in DMF could be estimated on the basis of direct supermolecular approach consisting in calculating the LUMO energies for DMF-silane complexes. Although the formation of such complexes has been not only assumed but in some cases even proved spectroscopically<sup>32</sup>, there is no information about their detailed structure available so far. The use of this direct approach has thus to be excluded and the influence of specific solvation interactions can be estimated only indirectly by comparing the  $E_p$  values with the LUMO energies calculated in the isolated molecule approximation ( $\epsilon = 1$ ) on one hand and corrected for nonspecific electrostatic interactions of the polar DMF ( $\epsilon = 37$ ) on the other.

The influence of increasing polarity is manifested by the increase of the LUMO energies in the series of chlorosilacyclobutanes as well as their acyclic analogues. If the solvation effect of DMF were therefore restricted only to nonspecific electro-

static interactions included in the solvaton model, one could expect an increasing resistance to the reduction in comparison with anisole. This theoretical expectation is, however, in accord with experiments only in the series of chlorosilacyclobutanes, whereas in the series of acyclic chlorosilanes the reduction in DMF is easier than in anisole. Such a disagreement between the theory and experiment for aliphatic chlorosilanes can be therefore regarded as arising just from the neglect of possible specific interactions in the solvaton model. Their influence manifests itself not only in the reversal of experimental reducibility of cyclic and acyclic chlorosilanes but also in the inversion of the trends in the values of reduction potentials  $E_p$  in dependence on the number of chlorine atoms (Table II).

We are of course aware of the fact that such an interpretation of the deviations of experimental  $E_p$  values from the predictions of the solvaton model represents only an indirect evidence for the hypothesis about specific solute-solvent interactions in DMF. It would be therefore interesting to verify the conclusions of the above theoretical analysis by direct experimental study of the stability of the corresponding complexes.

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