P8

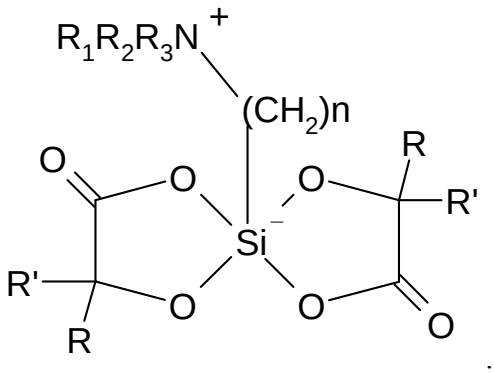
A Study of the Hydrolitical Stability of Spirobi(1-sila-2,5-dioxacyclopentan)ates

Kristians Ostrovskis
Faculty of Materials Science and Applied Chemistry, Riga Technical University, Azenes Str. 14/24, Riga, LV-1007, Latvia
e-mail: Kristians.Ostrovskis@rtu.lv

The most interesting compounds in class of spirobi(1-sila-2,5-dioxacyclopentan)ates are electrostatically stabilized silanates (ES-silanates). The first representative of these silanates was obtained at the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR (at present, the Latvian Institute of Organic Synthesis) in 1982 [1].

Erchak et al. [2, 3] have shown that the stabilization of ES-silanates is provided by their trigonal bipyramidal structure. The same conclusion was obtained by calculation on the basis of crystal field theory. This has been shown in the work [4]. Of course, this conclusion concerns a qualitative explanation of the stability of ES-silanates. Crystal field theory cannot be used for the quantitative determination of such systems. Therefore, it is necessary to provide the calculation of the hydrolysis reaction coordinate and quantitative determination of the activation energy, as well as study of the factors affecting the stability of ES-silanates.

The aim of the investigation is the estimation of the activation energy of hydrolysis reaction using the molecular orbital method. In the present research, the silanates with following common formula have been considered:



Comparing a series of related silanates, the Bell–Evans–Polyani (BEP) principle has been used for the qualitative estimation of activation energy, from which the linearity rule for the free energies follows [5].

Figure 1 schematically shows the BEP diagram for the process of hydrolysis of the compounds **1** (R=R'=R_1=H, R_2=R_3=CH_3, n=1) and **2** (R=R'=R_1=H, R_2=R_3=CH_3, n=2).

This diagram illustrates that the activation energy (E_a) is significantly higher for silanate **1**. Such estimates of activation energy have been fulfilled for series of previously synthesized silanates.

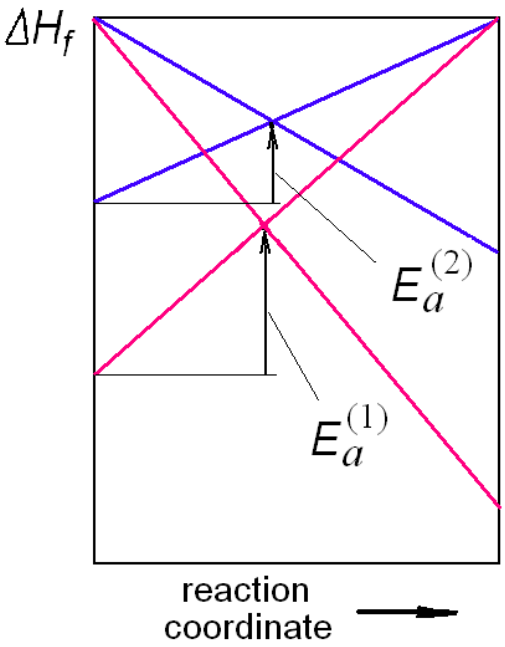


Figure 1. BEP diagram for the hydrolysis reaction of silanates

Supervisors: *Dr.phys. S.Belyakov,*
Dr.chem. M.Fleisher.

References

[1] Erchak, N.P.; Lukevics, E.Ya.; Matorykina, V.F.; Kemme, A.A.; Bleidelis, Ya.Ya. USSR Inventor's Certificate 1059872 (1983); *Byul. Izobret.*, No. 45, 239 (1983).
[2] Erchak, N.P.; Ancens, G.; Kemme, A.; Lukevics, E. in: *XI International Symposium on Organosilicon Chemistry*, Université Montpellier II, France (1996), PA60.
[3] Erchak, N.P. *Author's Abstract of Chemical Sciences Doctoral Dissertation*, Irkutsk (1991).
[4] Belyakov, S.; Erchak, N.P.; Zheimote, S.; Fleisher, M.; Lukevics E. *Chemistry of Heterocyclic Compounds,* **2008**, *44,* 1520–1526.
[5] Dewar, M.J.S.; Dougherty, R.C. *The PMO Theory of Organic Chemistry*, Plenum Press, New York (1975).