THE REACTIVITY OF ALKOXYSILANES STUDIED BY METHODS OF THEORETICAL CHEMISTRY

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A molecular geometry, a distribution of electron density and indices of reactivity of fifteen derivatives of alkoxysilanes $Si(OH)_x(OCH_3)_y(OC_2H_5)_z$, $(x+y+z=4)$ *were calculated by semiepirical quantum-chemical MNDO method, with an aim to study their ability to undergo the hydrolysis reactions: The highest reactivities were obtained for tetramethoxy derivative for both possible reaction mechanisms, nucleophilic and electrophilic.*

INTRODUCTION

At the present time the sol-gel process is a promising route to the production of new materials with important properties, which are often not possible to prepare by classical methods. The methods where as starting materials are used alkoxysilanes have a very important role.

The first reaction in this process is the hydrolysis of alkoxysilanes. The hydrolysis may influence the course of the consecutive reactions and also the formation of final products. From this point of view it is interesting to ascertain the effect of the nature of the alkoxygroup and of the degree of hydrolysis, on the reactivity of individual partially hydrolysed species.

There are well-known experiments to determine the kinetics of hydrolysis of alkoxysilanes (especially using NMR spectroscopy) [1–6]. Because the hydrolysis is the fastest from all the reactions, its study is very difficult. There is impossible to detect the individual degrees of the hydrolysis because reactions proceed too quickly. Therefore, all the kinetic models cited suppose the equal reaction rate constant per one R-group for all degrees of hydrolysis [1–6]. This assuption is contradictory to general chemical reasoning [7].

Burggraf and Davis [8] have modelled nucleophilic catalysed hydrolysis by theoretical study of the nucleophilic attack of $Si(OH)_4$ associated with the formation of pentacoordinate activate complex and consecutive elimination of water molecule and condensation. They showed by comparison with ab initio study of model systems [9] the adequacy of the use of semiepirical methods of MNDO-type for the study of systems of this type.

Both, the differently substituted alkoxysilanes and the products of their partial hydrolysis, can serve as a starting point of the polycondensation. The present paper is therefore directed to the study of electron structure of such a systems. At the same time, the next aim is also to estimate, on the basis of reactivity indices, the relative ability of individual studied compounds to enter the reactions of different types and mechanisms.

METHOD

The calculations were performed by MNDO (Modified Neglect of Differential Overlap) method [10], using a version of program which enables the optimization of molecular geometry. The starting molecular geometries were obtained by using of standard values of bond lengths and valence angles [11], considering the molecules in zig-zag conformation. There were optimized all internal geometrical degrees of freedom, except the bond lengths and valence angles of hydrogens of alkyl groups. Dihedral angles of hydrogens of alkyl groups were optimized in a such way, that mutual position of hydrogen atoms, bonded to the same carbon atom, were unchanged.

RESULTS AND DISCUSSION

For presentations of results in tables abbreviations according to Fig.1 are used.

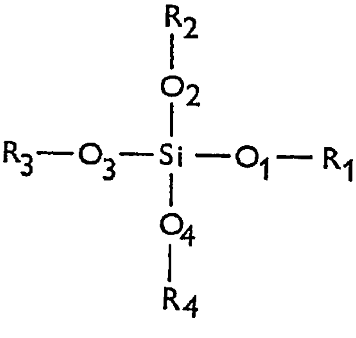

Fig. 1: R_1 *= H, M, E. H = hydrogen, M = methylgroup, E = ethylgroup. Abreviation used in Tables:* $R_1R_2R_3R_4$ *e.g. HMME means* $Si(OH)(OCH_3)_2(OC_2H_5)$

Table I

Bond lengths [10^{-10}m]

	Si-01	Si-02	Si-03	Si-04
MMEH	1.703	1.698	1.697	1.700
MEEE	1.698	1.701	1.700	1.700
EEEE	1.696	1.699	1.699	1.699
MMMH	1.704	1.698	1.697	1.698
MMHH	1.702	1.702	1.699	1.699
MMMM	1.698	1.698	1.697	1.698
EEEH	1.702	1.701	1.698	1.700
MMEE	1.699	1.697	1.699	1.701
EEMH	1.703	1.697	1.700	1.701
MMME	1.698	1.697	1.697	1.700
MEHH	1.703	1.700	1.699	1.702
EHHH	1.707	1.707	1.630	1.703
MHHH	1.704	1.704	1.704	1.700
HHHH	1.702	1.700	1.700	1.702
EEHH	1.700	1.702	1.702	1.701

Table II

Valence angles

	<01	<02	<03	<04
MMEH	120.8	131.2	131.2	129.9
MEEE	131.7	130.0	130.2	130.4
EEEE	131.1	130.9	130.8	131.1
MMMH	120.0	131.1	131.0	131.1
MMHH	120.8	120.8	130.8	130.8
MMMM	131.3	131.5	131.6	131.4
EEEH	129.8	110.0	130.0	130.0
MMEE	129.9	131.3	130.4	110.0
MEEH	129.8	131.2	129.9	110.0
MMME	131.4	131.6	131.6	129.7
MEHH	120.0	120.0	130.9	110.0
EHHH	119.2	120.5	127.3	129.4
MHHH	120.6	120.6	120.6	130.1
HHHH	121.0	122.1	122.0	121.5
EEHH	120.8	129.8	129.3	129.5

Table I shows some important bond lengths from obtained optimized bond lengths. The bond lengths Si-O vary from 1.697 to 1.704 × 10^{-10}m. These are well corresponding with experimental data and with results of calculations for various systems which contain this bond [12,13,14,16,17].

The obtained bond lengths O-H span the interval 0.923–0.960×10^{-10}m. They correspond very well with results of calculations by ab initio methods [12,16]. The bond lengths O-C vary from 1.380 to 1.385 × 10^{-10}m.

Some important valence angles are in Table II. The valence angles centered at oxygens are about 120°, if the hydrogen atom is bonded to oxygen. For oxygen

Table I

Bond lengths [10^{-10}m] – continue

	01-R1	02-R2	03-R3	04-R4
MMEH	0.932	1.380	1.381	1.383
MEEE	1.381	1.385	1.383	1.383
EEEE	1.387	1.383	1.383	1.383
MMMH	0.923	1.380	1.378	1.381
MMHH	0.933	0.933	1.381	1.381
MMMM	1.380	1.380	1.381	1.381
EEEH	0.932	1.384	1.384	1.383
MMEE	1.381	1.380	1.384	1.385
MEEH	0.933	1.381	1.384	1.384
MMME	1.381	1.380	1.381	1.385
MEHH	0.960	0.932	1.375	1.384
EHHH	0.960	0.930	0.960	1.380
MHHH	0.933	0.933	0.933	1.381
HHHH	0.932	0.932	0.932	0.933
EEHH	0.933	0.933	1.384	1.383

Table II

Valence angles – continue

	01-Si-02	01-Si-03	01-Si-04
MMEH	111.8	104.9	129.9
EEEH	111.7	104.9	112.0
EEEE	108.7	110.3	107.9
MMMH	111.9	105.0	110.8
MMHH	111.0	104.9	111.1
MMMM	111.5	105.2	111.6
EEEH	112.1	104.8	110.8
MMEE	111.8	105.1	111.8
MEEH	112.0	104.9	111.0
MMME	111.6	105.1	111.9
MEHH	111.2	104.8	111.1
EHHH	110.3	105.8	109.9
MHHH	110.2	106.0	110.1
HHHH	108.4	108.6	111.2
EEHH	111.0	104.8	111.2

Table IV

Net charges

	Si	01	02	03	04
MMEH	1.4269	-0.5830	-0.5830	-0.5749	-0.5695
MEEE	1.4493	-0.5797	-0.5640	-0.5653	-0.5664
EEEE	1.4477	-0.5643	-0.5716	-0.5779	-0.5709
MMMH	1.4298	-0.5333	-0.5823	-0.5693	-0.5821
MMHH	1.4033	-0.5350	-0.5342	-0.5864	-0.5860
MMMM	1.4631	-0.5768	-0.5782	-0.5786	-0.5778
EEEH	1.4190	-0.5387	-0.5694	-0.5620	-0.5706
MMEE	1.4516	-0.5766	-0.5777	-0.5668	-0.5633
MEEH	1.4229	-0.5377	-0.5748	-0.5701	-0.5693
MMME	1.4570	-0.5779	-0.5790	-0.5788	-0.5623
MEHH	1.3947	-0.5319	-0.5361	-0.5829	-0.5711
EHHH	1.3953	-0.5369	-0.5561	-0.5774	-0.5733
MHHH	1.3713	-0.5386	-0.5452	-0.5398	-0.5823
HHHH	1.3498	-0.5444	-0.5501	-0.5513	-0.5581
EEHH	1.3926	-0.5347	-0.5351	-0.5726	-0.5740

atoms bonded to alkyl group these angles are about 130° in all the studied cases. While the angles Si-O-H are in very good agreement with results of other authors, the angles Si-O-C have higher values than analogous angles in similar systems [10,11,13,14,15,18,19]. It is necessary to consider that our systems were chemically different from systems studied in the cited papers. It is well-known that potential surface, connected with the change of Si-O-R angle has a very shallow minimum [20]. This geometrical degree of freedom has considerable flexibility and it may be very strongly dependent on the actual chemical environment of the given centre.

Table III contains some important dihedral angles

Table III

Digedral angles

	<01	<02	<03	<04
MMEH	54.8	0	299.1	178.2
EEEM	57.6	108.0	300.0	180.0
EEEE	178.4	52.0	173.0	293.9
MMMH	301.4	0	60.4	181.8
MMHH	299.5	59.6	179.3	0
MMMM	0	58.0	179.1	300.6
EEEH	58.4	179.9	299.7	177.9
MMEE	300.6	58.0	178.8	180.0
MEEH	301.6	60.5	181.8	180.1
MMME	299.7	178.2	57.0	180.0
MEHH	299.5	59.7	179.3	180.0
EHHH	300.3	0	58.4	179.5
MHHH	58.5	0	300.2	179.4
HHHH	0	296.1	175.5	55.7
EEHH	59.5	299.7	180.0	179.2

Table IV

Net charges - continue

	R1	R2	R3	R4
MMEH	0.2087	0.2776	0.2789	0.2202
MEEE	0.2810	0.2193	0.2210	0.2214
EEEE	0.2257	0.2257	0.2242	0.2261
MMMH	0.2077	0.2772	0.2767	0.2795
MMHH	0.2095	0.2098	0.2792	0.2769
MMMM	0.2771	0.2802	0.2804	0.2797
EEEH	0.2083	0.2195	0.2194	0.2208
MMEE	0.2789	0.2800	0.2213	0.2189
MEEH	0.2800	0.2804	0.2804	0.2178
MMME	0.2800	0.2804	0.2805	0.2184
MEHH	0.2111	0.2099	0.2768	0.2178
EHHH	0.2083	0.2065	0.2278	0.2179
MHHH	0.2089	0.2087	0.2086	0.2760
HHHH	0.2120	0.2126	0.2162	0.2140
EEHH	0.2091	0.2088	0.2187	0.2196

Table V

HOMO and LUMO energies

	HOMO	LUMO	Δ
MMEH	-11.1087	-0.9541	-10.1546
MEEE	-10.9328	-1.0121	-9.9207
EEEE	-10.9486	-0.9700	-9.9786
MMMH	-11.1703	-0.9826	-10.1261
MMHH	-11.3522	-0.8812	-10.4710
MMMM	-11.0692	-1.0583	-10.0109
EEEH	-11.0110	-0.9167	-10.1943
MMEE	-10.9867	-1.0230	-9.9637
MEEH	-11.0740	-0.9355	-10.1385
MMME	-11.0239	-1.0362	-9.9877
MEHH	-11.2890	-0.8717	-10.4173
EHHH	-11.3148	-0.6674	-10.6474
MHHH	-11.5179	-0.7904	-10.7275
HHHH	-12.0283	-0.6310	-11.3974
EEHH	-11.2325	-0.8458	-10.3867

for systems, where these parameters have a meaning for a global definition of molecular geometry.

The net charges of important atoms for studied systems are in Table IV. The positive charge of Si atom increases with the number of methyl groups and is the highest in case of tetramethoxy derivative. The charge of Si atom of ethoxyderivatives is lower than for other derivatives in all cases. The negative charges of oxygen atoms increase in the order -OH, -OC_2H_5, -OCH_3. There is an evident trend of a growth of positive charge of hydrogen of hydroxyl with a number of present hydroxy groups. The numerical values of the charges of the silicon and oxygen atoms are in agreement with the distributions of the charges, obtained for similar systems by semiempirical and ab initio STO-3G calculations [21].

Table V shows the values of the energy of the highest occupied molecular orbital (HOMO), of the lowest unoccupied molecular orbital (LUMO) and thier differences. The difference HOMO-LUMO grows, energy of HOMO decreases and LUMO energy grows with increasing number of hydroxy groups.

The LUMO energy is in all cases negative so all the studied systems should be able to interact with the nucleophilic reagents.

Table VI shows the bond-orders, expressed by Wiberg's indices [22]. The Si-O bonds are stronger in the case of the O-H group than in case of alkoxygroup. On the other hand the O-H bonds are weaker than O-alkyl ones. The Si-O bonds have a little lower bond orders than bonds O-alkyl.

Since the negative values of LUMO energies suggest a readiness to nucleophilic reactions, the values of nucleophilic superdelocalizabilities [23] were calculated. This may be extraordinary usefull for determination of trends in series of similar molecules. They are shown in Table VII. The carbon atoms, bonded to oxygen, have the highest values of this index of reactivity. These values are about 0.44 without a sig-

Table VI

Wiberg's indexes

	Si-01	Si-02	Si-03	Si-04
MMEH	0.8190	0.7642	0.7765	0.7689
MEEE	0.7691	0.7780	0.7740	0.7735
EEEE	0.7992	0.7687	0.7697	0.7696
MMMH	0.8209	0.7650	0.7764	0.7695
MMHH	0.8231	0.8247	0.7602	0.7593
MMMM	0.7720	0.7722	0.7716	0.7716
EEEH	0.8178	0.7683	0.7793	0.7673
MMEE	0.7707	0.7712	0.7739	0.7763
MEEH	0.8182	0.7760	0.7681	0.7689
MMME	0.7714	0.7708	0.7709	0.7774
MEHH	0.8260	0.8235	0.7556	0.7656
EHHH	0.8163	0.8053	0.8240	0.7568
MHHH	0.8183	0.8108	0.8166	0.7696
HHHH	0.8206	0.8108	0.8217	0.8077
EEHH	0.8235	0.8222	0.7643	0.7618

Table VI

Wiberg's idexes - continue

	01-R1	02-R2	03-R3	04-R4
MMEH	0.9359	0.9609	0.9592	0.9565
MEEE	0.9599	0.9561	0.9564	0.9564
EEEE	0.9477	0.9556	0.9527	0.9559
MMMH	0.9367	0.9607	0.9629	0.9596
MMHH	0.9359	0.9357	0.9603	0.9614
MMMM	0.9602	0.9590	0.7952	0.7916
EEEH	0.9361	0.9566	0.9560	0.9570
MMEE	0.9606	0.9602	0.9558	0.9557
MEEH	0.9360	0.9596	0.9567	0.9562
MMME	0.9596	0.9596	0.9595	0.9587
MEHH	0.9351	0.9355	0.9662	0.9564
EHHH	0.9368	0.9368	0.9233	0.9615
MHHH	0.9362	0.9358	0.9363	0.9614
HHHH	0.9351	0.9340	0.9330	0.9341
EEHH	0.9361	0.9362	0.9366	0.9576

Table VII

Nucleophilic superdelocalizabilities

	Si	01	02	03	04
MMEH	0.1231	0.1038	0.0004	-0.0051	-0.0002
MEEE	0.1546	0.0073	0.0058	0.0070	0.0077
EEEE	0.1256	0.0021	0.0018	0.0022	0.0017
MMMH	0.1399	-0.0153	0.0036	-0.0017	0.0039
MMHH	0.0803	-0.0344	-0.1008	-0.0106	0.0955
MMMM	0.1732	0.0109	0.0110	0.0112	0.0104
EEEH	0.1039	-0.0211	-0.0050	-0.0164	-0.0040
MMEE	0.1594	0.0076	0.0091	0.0084	0.0061
MEEH	0.1142	-0.0197	-0.0067	-0.0036	-0.0036
MMME	0.1637	0.0090	0.0092	0.0097	0.0077
MEHH	0.0787	-0.0339	-0.0334	-0.0096	-0.0132
EHHH	-0.1161	-0.0897	-0.0793	-0.0549	-0.0628
MHHH	0.0179	-0.0525	-0.0457	-0.0508	-0.0322
HHHH	-0.1419	-0.0975	-0.0945	-0.0933	-0.0929
EEHH	0.0601	-0.0382	-0.0390	-0.0165	-0.0161

nificant effect of other substituents.

The nucleophilic superdelocalizability of silicon atom is the highest in the case of the tetramethoxyderivative. It is decreasing with increasing number of ethoxy groups until reaching the value of tetraethoxyderivative. A significant decrease of this index of reactivity is seen for the hydroxyderivatives.

The obtained trends of the considered index of reactivity show that the carbon atom of the alkyl group, bonded with oxygen, will be a place of attack by an uncharged nucleophilic reagent (H_2O, NH_3, alcohol). In a case of anionic nucleophillic reagent (OH^-, F^-) a silicon atom may be a place of an attack, if we are looking at distribution of charge. Tetramethoxyderivative will have the highest reactivity. In the case of the attack on the carbon atom of the alkoxy group the O-R bond will be split. On the other hand for the centre of reactivity on the silicon atom the Si-O bond will be broken. Because the differences of bond orders are small, it is impossible to decide which mechanism will be more probable.

Table VII

Nucleophilic superdelocalizabilities - continue

	R1	R2	R3	R4
MMEH	0.0947	0.4409	0.4392	0.4391
MEEE	0.4370	0.4402	0.4386	0.4383
EEEE	0.4236	0.4307	0.4319	0.4297
MMMH	0.0958	0.4437	0.4408	0.4389
MMHH	0.0955	0.0952	0.4357	0.4394
MMMM	0.4438	0.4396	0.4405	0.4411
EEEH	0.0938	0.4372	0.4395	0.4364
MMEE	0.4393	0.4375	0.4400	0.4370
MEEH	0.0944	0.4379	0.4370	0.4393
MMME	0.4391	0.4392	0.4390	0.4416
MEHH	0.1017	0.0950	0.4398	0.4375
EHHH	0.0964	0.0864	0.0900	-0.0628
MHHH	0.0936	0.0906	0.0935	0.4391
HHHH	0.0869	0.0859	0.0863	0.0874
EEHH	0.0945	0.0948	0.4349	0.4359

It is evident from the trends of charge distribution on the oxygens that the oxygen, bonded to methyl group, will be the most reactive in the case of an electrophilic attack.

The experimental comparisons of the rate of the acid hydrolysis of tetramethoxy and tetraethoxysilane [6,24] endors this trend.

The slower hydrolysis of TEOS as opposed to TMOS is explained by differences in steric properties of their alkyl groups. Our calculations showed that also the effects of electron distribution play an important role.

The lower values of the positive charge on the silicon atom for the ethoxyderivatives (in contradiction with chemical intuition, which will ascribe greather electrondonor effect to OC_2H_5 group) show, that the hydrolysis would be faster for tetramethoxysilane than for tetraethoxysilane. The superposition of electron and steric effects may explain why the differences of the rate of hydrolysis of both TMOS and TEOS were higher than we can be expected solely on the basis of their steric effects.

The experimental measuring of kinetics of hydrolysis by ^{29}Si NMR spectroscopy endors this trend [6].

CONCLUSIONS

The calculated charges and indices of reactivity indicate the possibility of both nucleophilic and electrophilic attack. For any of these possible mechanisms the methoxyderivative shows the maximal reactivity. The use of semiempirical quantum-chemical method MNDO enabled the separation of the effect of electron structure and the steric effects on the kinetics of hydrolytic reactions of alkoxysilanes. Because of the polarity of the studied systems the more detailed study should include also the influence of environment by application of different solvatation models. Moreover, we suppose that it will be useful to extend such a study also in the area of consecutive condensation reactions.

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REAKTIVITA ALKOXYSILÁNOV ŠTUDOVANÁ METÓDAMI TEORETICKEJ CHÉMIE

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Semiempirickou kvantovochemickou metódou MNDO sa študuje molekulová geometria, elektrónová distribúcia a statické indexy reaktivity pätnástich derivátov alkoxysilánov $Si(OH)_x(OCH_3)_y$ $(OC_2H_5)_z$, $(x + y + z = 4)$, s cieľom študovať ich schopnosť podliehať hydrolytickým reakciám. Zvolené modelové systémy predstavujú ako východiskové látky prekurzorového spôsobu prípravy nových materiálov, tak aj možné medziprodukty, ktoré sa zúčastňujú reakcií, prebiehajúcich pri tomto procese. Najvyššie reaktivity sa získali pre tetrametoxyderivát pre oba možné reakčné mechanizmy ich hydrolýzy (nukleofilný i elektrofilný). Ukazuje sa, že za rozdiely v reaktivite etoxy- a metoxysilánov zodpovedajú nielen sterické, ale vo výraznej miere aj elektrónové faktory.

Obr. 1.: $R_i = H,M,E$, *H = vodík, M = metylová skupina, E = etylová skupina. Označenie použité v tabuľkách:* $R_1R_2R_3R_4$ *napr. HMME znamená* $Si(OH)(OCH_3)_2(OC_2H_5)$