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Evaluation of Bonded Layer Disorder from Thermodynamic Behavior of Methylaminopropyl Groups Immobilized on SiO_2

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SUMMARY: Thermodynamic characteristics of reaction between proton and methylaminopropyl groups that are covalently bonded to silica gel surface were calculated. First evidence of short-distance interaction between neighboring bonded amines was obtained. Addition of the first proton does not destroy such interaction. Second proton promotes significant geometry changing.

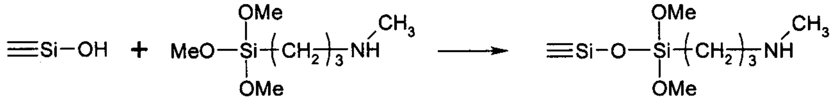
Introduction

Determination of acid-base properties of immobilized organic compounds is actual task for evaluation of chromatographic and analytical properties of new adsorbents. Despite of several publications in this field many unsolved problems remain (1). The main is unclear behavior of bonded groups in highly polar media. It is known that most donor ligands that are covalently bonded to solid surface when dry have collapsed structure in interfacial layer (2). But there is some evidence that in polar liquid media geometry of bonded layer can be changed from collapsed to extended (2). It is unclear how this changing reflects to properties of bonded groups. No research was made to monitor changing in geometry of bonded layer while modified solids react in water media, especially at different temperature.

This research was an attempt to investigate changing in geometry of methylamine bonded layer during reaction of modified silica with water solution of strong acid through determination of protolytic constants at various temperature.

Results

Methylaminopropyl silica gel (Sg-$NHCH_3$, CL=0.623mM/g) that was used for investigation was obtained by silylation of bulk dry silica in toluene, according to the reaction:



$$\equiv Si-OH + MeO-\underset{OMe}{\overset{OMe}{Si}}-(CH_2)_3-NH-CH_3 \longrightarrow \equiv Si-O-\underset{OMe}{\overset{OMe}{Si}}-(CH_2)_3-NH-CH_3$$

CCC 1022-1360/98/$ 17.50

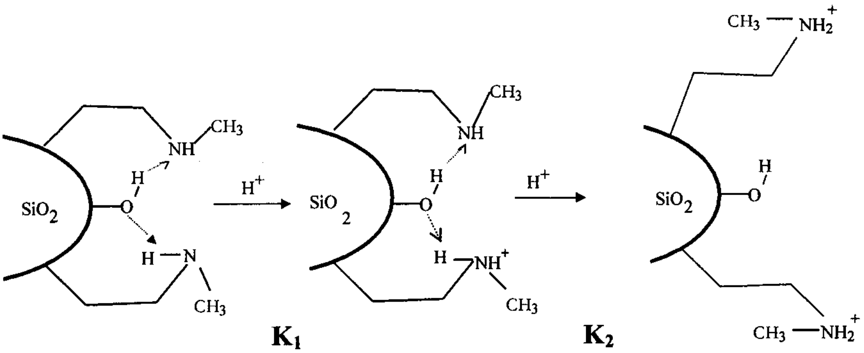
Concentration of bonded groups determined from elemental analysis ($0.62 mmol \cdot g^{-1}$) was in good agreement with that obtained from pH titration. High ionic strength created by NaCl was used to reduce influence of changing in surface potential during protonation of bonded groups. For this, modified silica gel was introduced for 12 h into solution of NaCl ($5 \cdot 10^{-2}$ $mol \cdot l^{-1}$) and then hydrochloric acid was added dropwise. The experimental temperature was changed from 20 to 50°C. For determination of equilibrium constants a model of "chemical reactions" was used [1)]. This model utilizes a nonlinear method of least squares and handling sorption isotherms.

It is known that reaction of bonded amines with hydrogen can not be described as a single-step process as it is in solution [1,3-4)]. At least two equilibrium constants should be utilized instead. In our experiment additional evidence was obtained for this fact. In all experiments equilibrium could be correctly described with two constants only, see Tab. 1.

Tab. 1. Protolytic constants (K_1 and K_2) of Sg-$NHCH_3$ at different temperatures

constants	Temperature, K			
	293	305	311	323
lgK_1	3,40	3,34	3,40	2,95
lgK_2	6,61	6,53	6,44	6,23

Few models were developed to explain this behavior of bonded groups. In the term of "chemical reactions" this particularity is explained as conjugation of bonded groups into associates. In this case first proton reacts with one from any amino groups in associate and reduces affinity of the proton for the second group. Since such reduction can not be explained as charge-transfer through alkyl chain (it is too long), short-distance interaction between neighboring amines is assumed, see scheme below:



Nevertheless no evidence was obtained for such scheme. To verify the scheme of an interaction between bonded amines and hydrogen ions, thermodynamic parameters of the reaction were calculated. For this, equilibria constants of the reaction were determined at various temperatures. From linear correlation observed between inverse temperature and equilibrium constants invariability of the interaction was concluded. It means that properties of bonded groups and amines in solution change with temperature similarly. In other words no geometry changing take place for bonded groups with temperature increase. For both correlations: $\log K_1 = 1300/T - 0.9$ ($r^2 = 0.61$) and $\log K_2 = 1200/T + 2.57$ ($r^2 = 0.92$) the slopes are almost identical. So protonation enthalpy for different types of bonded groups does not differ among themselves ($\Delta H_1 = 22$ and $\Delta H_2 = 25$ kJ·mol^{-1}). It means that there are no bonded groups with different affinity to proton, all amino groups are nearly identical. In contrast, the entropy of the first and the second step of the reaction differ quite remarkably: -17 J/mol·K and +49 J/mol·K respectively, see scheme. Decreasing in entropy for the first stage of protonation indicates reduction in degree of freedom for the reacting proton. If during a reaction with bonded groups proton lost all three degrees of freedom, decreasing of entropy in $3R/2 = 12.5$ J/mol·K can be expected. It is in good agreement with observed value and supports the scheme proposed above. The interaction of second protons with bonded groups takes place with high positive entropy. It is clear that it indicates increasing in bonded layer disorder during this reaction. The same conclusion can be made from the scheme proposed above. Reaction of the surface associate with the second proton should initiate destruction of that associate due to repulsion of neighboring homopolar groups. From higher than expected value of entropy for the second step of the reaction, active migration of proton in interfacial layer can be predicted.

Conclusions

No changing in geometry of bonded layer was registered during holding of silica chemically modified with methylamine in water at different temperature. In two-step reaction of bonded groups with proton the latter promotes destruction of surface associates and essentially increases interfacial disorder.

References

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