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INFLUENCE OF NANOSILICA SURFACE ON THIONE-THIOL TAUTOMERISM OF GRAFTED THIOUREA GROUPS

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The thione-thiol tautomerism has been investigated of thiourea groups grafted to silica surface in the presence of water molecules. The configuration of the transition state has been calculated by quantum chemical modeling of a N, N'-dimethylthiourea (DMTU) molecule in the forms of $(CH_3)_2(NH_2)_2CS/CH_3NHCSHNCH_3$ and of fragment silica clusters $(HO)_3SiCH_2NHC(S)NHCH_3$ with one water molecule (density functional theory method, B3LYP/6-31G (d, p)). The value of the total energy of the transition state with one water molecule and the activation energy of the thione-thiol tautomeric transition for different conformations of the system were obtained. The results of these calculations have shown that the activation barrier in the presence of a silica matrix decreases. The activation barrier in the studied systems is higher than that in similar systems in vacuum.

Introduction

Thiourea derivatives have a wide spectrum of biological activities including antibacterial, antifungal, TB, antihelminthic, insecticidal, herbicidal effect and the properties of the plant growth regulator [1, 2-5]. Acidic solutions of thiourea were examined as an alternative to cyanide extraction of the precious metals due to their fast kinetics and low toxicity [6]. Complex compounds of thiourea are characterized by a very high and selective extraction and transportation Ag (I) in the presence of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) using the method of the gradient pH [7]. The first example ($CH_3C(O)NHC(S)NH_2$) of this class of molecules has been known for more than a century ago [7]. Acyl (aroyl) thiourea ligands were used for extraction of gold (III) [8].

It is known that compounds containing composition thiourea fragments [–NH–C(=S)–NH–] are good complexing compounds. Thiourea derivatives behave generally as flat ligands, where S and N atoms act as donors involved in coordination to the metal center. The substituted thioureas have, however, a greater diversity in the coordination chemistry, which are connected with their conformational isomers, steric effects, the presence of donor groups in substituted and intra-molecular interactions [1]. This capability of urea and thiourea moiety to form H-bond also contributes to the formation of gels [9]. Thiourea fragments can exist in two tautomeric forms - thione and thiol, [–NH–C(=S)–NH–] and [–N=C(SH)–NH–]. Various factors such as pH of the medium [7], the nature of the solvent [10, 11] have the greatest influence on the shift of the tautomeric equilibrium in either direction, as tautomeric transitions caused prototropic binary equilibrium. The high mobility of thione-thiol balance and speed of mutual transformations considered prototropic tautomeric forms leads to the fact that they rarely isolate in pure form and calculate the proportion. It should be added that the simple cations often unstable. Thiourea monomers that have been highlighted in the low-temperature argon matrix are solely thione tautomeric form [12]. Upon UV irradiation (I> 300 nm) there is a photo reaction, the result of which is to convert the initial isomer compound in its thiol tautomer [12]. This is only possible mechanism for the conversion of the ground state of the thiol form in thionyl at low temperature proton tunneling through very high energy barrier of 9030 cm^{-1} (108 kJ mol^{-1}) (MP2/6-31++G(d,p)). The structure of the photoproduction of species was determined by comparing the experimental spectra with the

theoretically calculated IR spectra obtained by DFT (B3LYP)/6-31++G(d,p) [12]. As one of the compounds containing thiourea fragments –NH–C(=S)–NH–, silica was used functionalized with thiourea groups [≡$SiCH_2NHC(S)NHCH_3$] [13]. So the question of the existence of the fragment shape on the silica surface [≡$SiCH_2NHC(S)NHCH_3$], and the influence of the surface and the water molecules on the process - both before and after the sorption process becomes important.

The aim of this work is the quantum-chemical analysis of the IR spectra of the surface layer of silica functionalized with thiourea groups [≡$SiCH_2NHC(S)NHCH_3$], which coexist in the Thione and thiol forms in the presence of water molecules. As a model of the ligand center molecule was chosen of the N, N'-dimethylthiourea (DMTU) in various forms and a surface fragment of [$(HO)_3SiCH_2NHC(S)NHCH_3$], simulating a trifunctional silane [$(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$], used in practice [13].

Experiments

IR spectra. FT-IR spectra of synthesized materials [13] were recorded on a Thermo Nicolet Nexus Fourier-transform infrared spectrometer in the 400–4000 cm^{-1} range, working in ‘‘Nexus Smart Collector’’ mode with a resolution of 8 cm^{-1}. The samples were previously ground with solid KBr (Fluka, for IR spectroscopy). The sample/KBr mass ratio was 1/30. The spectra were analyzed using software ‘‘OMNIC’’.

Quantum chemical calculations. Quantum chemical calculations on the total energy of the optimized geometrical structures of thione and thiol forms of N, N'-dimethylthiourea and of the fragment $(HO)_3SiCH_2NHC(S)NHCH_3$ were performed using density functional theory method (DFT) [14] and the hybrid B3LYP potential [15] with basis set 6-31G (d, p).

Such calculation methods have been successfully used for the interpretation of the vibrational spectra are similar in chemical structure of compounds (proton transfer processes in thiourea) [12].

The calculated vibrational frequencies in the IR spectra were used as scaled by a factor of 0.95. Calculations were performed by means of the software package PC GAMESS [16] (version FireFly 8.0.0 (http://classic.chem.msu.su/gran/firefly/index.html) by A.Granovsky).

Results

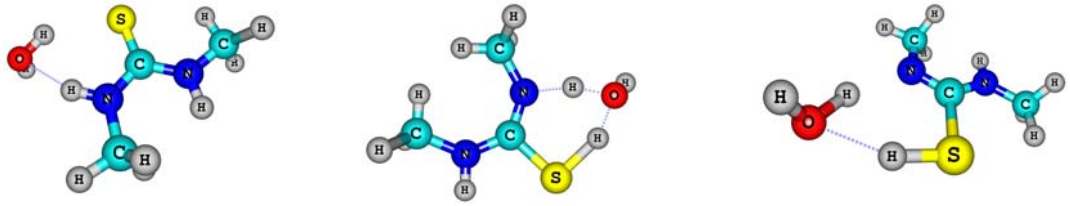
The spectrum of tetraethoxysilane (TEOS) was recorded in liquid form between KRS plates [13]. The vibrational spectra (IR and Raman) regularly provide useful information on the electronic structure and the conformation of the molecule. Information about the research focused on the probable correlations between the IR and Raman spectra of the studied thiourea derivatives and their capability to form complexes with heavy metal ions exists in the literature [1]. This group of compounds was tested as ionophores in ion-selective electrodes [17].

Note that the analysis of the IR spectra of the complexes formed in the surface layer of mesoporous silicas with complexing group structure ≡$Si(CH_2)_3NHC(S)$ NHC_2H_5 was found to have not single but two absorption bands, which are connected with taking part in the coordination group -NH-C(S)-NH- [18]. Note also that in obtaining mesoporous sorbent with thiourea groups by templating method [8, 18, 19] of mesophase surfactant removal can be carried out under different conditions - refers to the nature of the solvent, the acidity of the environment. This, in turn, may account for the appearance on the support surface of tautomeric equilibrium which can stabilize the surface. Since the above assumption was based on the analysis of the IR spectra, it is noted that the thiourea moiety has no distinct characteristic absorption band [13]. The absorption band at ~ 1560 cm^{-1} is generally identified by the fragment due to the contribution of several oscillations. The absorption bands corresponding to stretching vibrations ν (C = S) form or thionyl ν (S-H) thiol, have a low intensity. Therefore, the low content of fixed thiourea ligand (which is typical for the vast majority of sorbents), their identification is difficult also for these absorption bands. It becomes even more problematic if

the content of the thiol tautomer is substantially minimal as compared to thione one. Finally, if the absorption band at ν (S-H) is in 2560 cm^{-1}, in which the absorption bands of other ligands fixed very rarely, the absorption band at ν (C = S), located in the IR spectrum at ~ 630 cm^{-1}; It can often be masked by other absorption bands.

As it well known, organic compounds, containing thiourea group such as -NH-C (= S)-NH- , can exist in two tautomeric forms - thione and thiol. Previously [20-22], we designed a model of silica surface layer formed due to hydrolytic polycondensation of three- and tetraalkoxysilanes. This silica surface considered bears grafted thiourea groups in thione form. In this article N, N'-dimethylthiourea groups were selected as models for thiourea complexing center in thione, thiol forms, transition state and a form where proton is substituted with sodium cation.

In this article molecule N, N'-dimethyl thiourea and molecular fragment $(HO)_3SiCH_2NHC(S)NHCH_3$ silica matrix with the presence of a single water molecule were selected as models. We also studied the effect of water molecules on the energy barrier of the thione-thiol transition. Configurations, total energy, and parameters of the optimized geometrical structure of various forms of N,N'-dimethylthiourea with one water molecule are presented in Fig. 1 and Table 1.



1 -703.28341 | 2 (TS) -703.23334 | 3 -703.25369

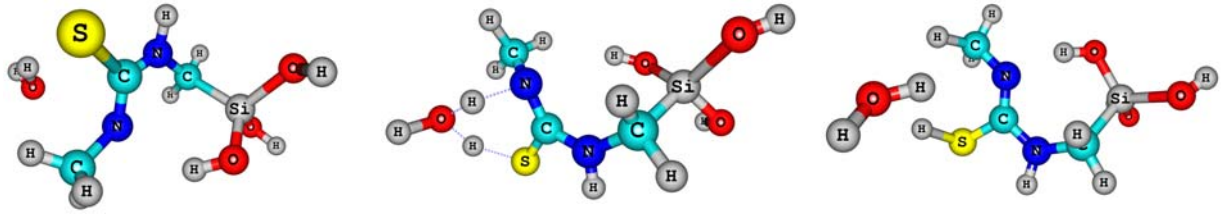
Fig. 1. The total energy calculated (E, a.u.) of the N, N'-dimethylthiourea (DMTU) with one water molecule in various forms: 1 - thione, 2 - transition state, 3- thiol.

Table 1. Parameters (bond lengths, Å; the angles, degrees) of the optimized geometrical structures of various forms of N, N'-dimethylthiourea (DMTU) with one water molecule*

	1	2 (TS)	3
		DMTU	
R_{SH}	-	1.630	1.370
R_{CS}	1.707	1.798	1.799
R_{CN}	1.349, 1.368	1.305, 1.376	1.282, 1.392
R_{NC}	1.459, 1.465	1.464, 1.449	1.456, 1.466
R_{CH}	1.092 - 1.095	1.098 – 1.091	1.090 - 1.098
R_{NH}	1.024, 1.010	1.012, 1.396	1.012
$<_{HSC}$	-	91.80	94.92
$<_{SCN}$	122.17, 119.17	115.17, 114.21	120.11, 112.29
$<_{NCN}$	118.66	130.62	127.59
$<_{CNH}$	114.04, 110.56	112.99, 113.60	112.07
$<_{NCH}$	107.88 – 112.99	107.55 – 118.31	107.93 – 112.81
		DMTU+H_2O	
$R_{S\text{-}HOH}$	2.374	1.27243	1.910
$R_{NH\text{-}OH2}$	1.891	1.12178	1.862
$<_{S\text{-}HO(H)}$	145.980	152.841	154.108
$<_{NH\text{-}O(H2)}$	163.406	159.578	156.365

*Structure numbers 1,2,3 are shown in Fig. 1.

In addition, for a molecular fragment $(HO)_3SiCH_2NHC(S)NHCH_3$, quantum chemical calculations were performed. Complexing site of this fragment is identical to that in the three functional silane $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$, which is widely used to produce of functionalized polysiloxane xerogels and mesoporous silicas [13]. Thus it considered thione (4), thiol form (6), and transition state (5) (see. Fig. 2 and Table 2).



4 -1219.80078 | 5 (TS) -1219.72693 | 6 -1219.77830

Fig. 2. The calculated total energy (E, a.u.) of molecular fragment $(HO)_3SiCH_2NHC(S)NHCH_3$ with one water molecule in various forms: 4 - thione, 6- transition state and 5 – thiol.

Table 2. Parameters (bond lengths, Å; the angles, degrees) of the optimized geometry of molecular fragment $(HO)_3SiCH_2NHC(S)NHCH_3$ in various forms with one water molecule*

	4	5(TS)	6
		$(HO)_3SiCH_2NHC(S)NHCH_3$	
R_{SH}	-	1.653	1.353
R_{CS}	1.692	1.782	1.830
R_{CN}	1.352, 1.378	1.341, 1.352	1.286, 1.362
R_{NC}	1.466, 1.469	1.465, 1.486	1.467, 1.460
R_{CH}	1.095 - 1.092	1.092 – 1.098	1.093 - 1.096
R_{NH}	1.094	1.011, 1.38539	1.008
R_{SiO}	1.653 - 1.658	1.655 -1.662	1.646 - 1.665
<HSC	-	83.58	92.74
<SCN	120.70, 123.72	112.142, 126.87	111.48, 125.75
<NCN	115.55	120.25	122.77
<NCSi	115.28	115.92	117.33
<CSiO	111.99 - 112.25	101.88 – 113.29	101.30- 112.90
<CNH	113.65, 114.70	112.79, 94.617	114.84
<NCH	110.85, 107.11	106.26, 110.60	110.34, 106.93
<SiCH	107.37, 111.55	106.56, 109.76	107.99, 107.08
<OSiO	106.22 – 115.31	104.59 – 108.40	108.07 - 114.63
<SiOH	113.55 - 114.02	113.84 – 115.93	107.72- 115.57
		$(HO)_3SiCH_2NHC(S)NHCH_3+H_2O$	
$R_{S\text{-}HOH}$	2.497	1.178	2.249
$R_{NH\ldots OH2}$	4.207	1.181	2.444
$<_{S\text{-}HO(H)}$	162.074	152.22	139.775
$<_{NH\text{-}O(H2)}$	61.419	149.70	131.140

*Structure numbers 4,5,6 are shown in Fig. 2.

Discussion

The results of quantum chemical calculations on the total energy of the transition complex in vacuum and on the activation energy values of thione-thiol tautomeric transition between different conformations are shown in Fig. 3.

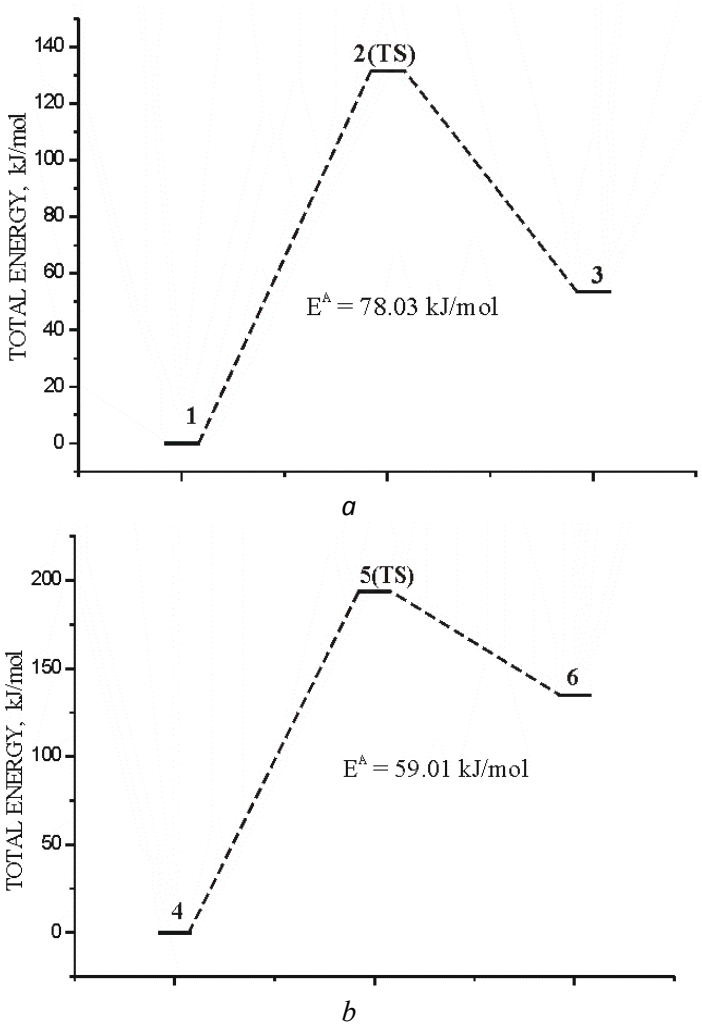


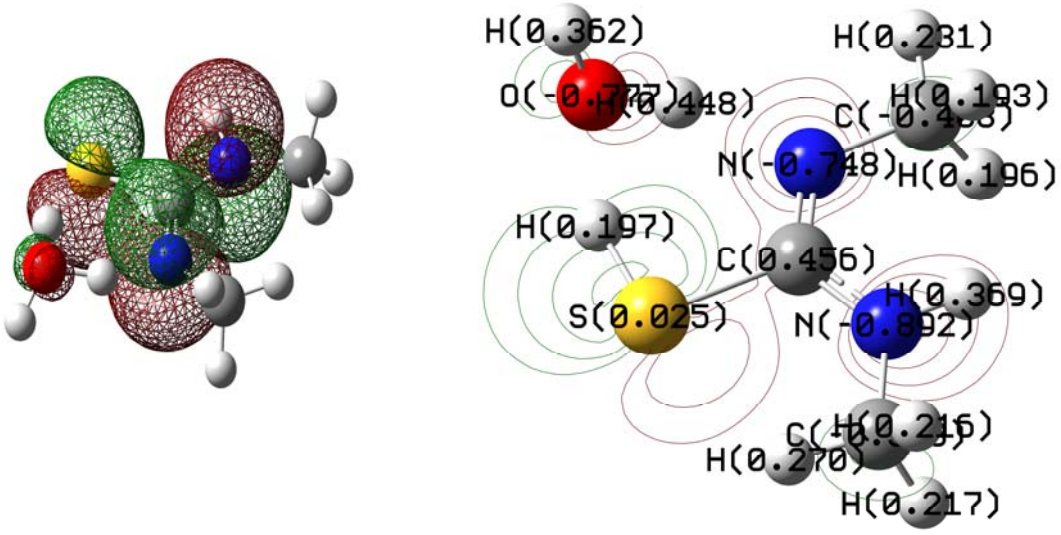
Fig. 3. Energy tautomeric transition diagram of N, N'-dimethylthiourea *(a)* and of fragment silica cluster with the functional group [-NHC(S)NH-] *(b)* (see text; the structures mentioned are enumerated correspondingly to those shown in Figs. 1 and 2).

Without water molecule, activation energy of the transition between the thione 1 and 2 forms of thiol N,N'-dimethylthiourea molecule was E^A = 69.05 kJ / mol [23], whereas in the presence of water molecules, it is E^A = 78.03 kJ / mol. Respectively, for a molecular fragment simulating the silica surface with a functional group [-NHC(S)NH-], this value was E^A = 47.52 kJ / mol in the case of transition 4 - 5 or E^A = 75,88 kJ / mol in the case of transition 4 - 5 ' [23], whereas in the presence of water molecules, it is E^A = 59.01 kJ / mol (Fig. 4). It is obvious that in the presence of water molecules, the activation barrier is reduced by participatory silica matrix. With respect to the vacuum system, the activation barrier is higher than that in the system involving a water molecule.

Analysis of the energy gap E between the frontier orbitals (22 α, β, 23 α, β and 53 α, β, 54 α, β) and charge distribution for the N, N'-dimethylthiourea of the molecule and the surface of the silica with the functional group [-NHC(S)NH-] in the presence of water molecules, can be used to determine the magnitude and electron donor and electron acceptor abilities of these compounds.

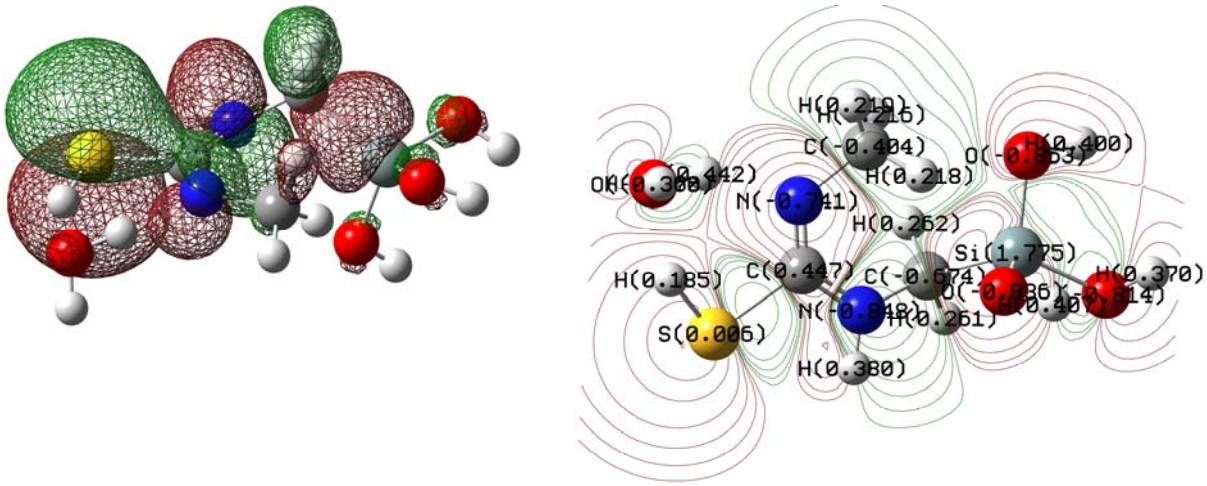
The charge distribution, and the surface contour of the upper surface of the occupied orbitals of N, N'-dimethylthiourea of the molecule (Fig. 4) and the surface of silica with the functional group [-NHC(S)NH-] (Fig.5) in the presence of water molecules are presented in Figs. 5, 6.

The surface shape of the last occupied orbital (23 - for the molecule N, N'-dimethylthiourea (Fig. 4 a) and 53 - for functionalized of groups [-NHC(S)NH-] silica surface interacting with a water molecule (Fig. 5 a) are different. It has a spherical shape in the first case, dumbbell - in the second case, which is caused by the influence of the silica matrix.



a *b*

Fig. 4. Occupied MO *(a)*; surfaces contours and charge distributions *(b)* for N,N'-dimethylthiourea molecule in the presence of water molecules.



a *b*

Fig. 5. Occupied MO *(a)*; surfaces contours and charge distributions *(b)* for molecular fragment simulating the silica surface with a functional group [-NHC(S)NH-] in the presence of water molecules.

As seen from the analysis of quantum chemical calculation of transition states (TS), complex molecule N,N'-dimethylthiourea and functionalized of groups [-NHC(S)NH-] silica surface interacting with a water molecule are flat, because all atoms lie in one plane and have sp^2 hybridization. Differences in the distribution of densities in the HOMO of N,N'-dimethylthiourea molecule (Fig.4 b), and silica surface functionalized by [-NHC(S)NH-] groups interacting with a water molecule are observed (Figure 5, b). In transition state, on the nitrogen atom which is H-bonded to the sulfur atom through a water molecule, there is a region of negative charge (indicated by green). On the second nitrogen atom covalently bonded to a hydrogen atom, there are areas of both positive and negative charges; on the

sulfur atom - positive charge (Fig. 4, b). In the presence of the silica matrix, on a nitrogen atom which is covalently bonded to and hydrogen through a spacer bound to a silicon atom, there is a region of negative charge (indicated by green). In transition state, on the nitrogen atom which is H-bonded to the sulfur atom through a water molecule, there is an area of positive charge (indicated in red). As shown in Figure 6b, on the oxygen atom in a water molecule is a region of negative charge, on the sulfur atom - positive. Interaction with the oxygen atom in the water molecule occurs at the point of tangency circuits electron density distribution of the nitrogen atom (positive), water molecules (negative), hydrogen and sulfur atoms (positive) (Fig. 5, b). Thus, the electron-acceptor ability of silica surface functionalized with groups [-NHC(S)NH-] interacting with a water molecule is considerably higher than the corresponding value for the molecule of N,N'-dimethylthiourea and both systems are characterized by a nitrogen atom which is H-bonded to the sulfur atom through a water molecule.

After analyzing the results of the calculations, it can be concluded that the presence of the silica matrix the band gap raises as compared with that of N,N'-dimethylthiourea molecule (E= 9.18 eV), in the presence of water molecules (E= 13.26 eV).

Thus, by quantum chemical calculations, one can see the effect of the silica matrix to change the distribution of the surface of the lowest occupied orbital, electron densities and the band gap of the molecule as compared to those of N,N'-dimethylthiourea.

Summary and conclusions

On the basis of quantum-chemical calculations performed to analyze the thione-thiol tautomerism, we can draw the following conclusions. In the systems of N, N'-dimethylthiourea in forms $(CH_3)_2(NH_2)_2CS$ / $CH_3NHCSHNCH_3$ / $CH_3NHCSNaNCH_3$ and the silica cluster fragment $(HO)_3SiCH_2NHC$ (S) $NHCH_3$ with a water molecule, the activation barrier is reduced by participatory silica matrix. With respect to the vacuum system, the activation barrier is higher than that in the system with a water molecule. Therefore, the lowest activation barrier of thione-thiol equilibrium is that in the presence of silica surface in vacuum.

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ВЛИЯНИЕ ПОВЕРХНОСТИ КРЕМНЕЗЕМА НА ТИОН-ТИОЛЬНУЮ ТАУТОМЕРИЮ ПРИВИТЫХ ГРУПП ТИОМОЧЕВИНЫ

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В работе была изучена тион-тиольная таутомерия тиомочевинных групп, привитых на поверхности диоксида кремния, в присутствии молекулы воды. Конфигурация переходного состояния была рассчитана путем моделирования молекулы N, N-диметилтиомочевины в формах $(CH_3)_2(NH_2)_2CS$ / $CH_3NHCSHNCH_3$ и фрагмента кластеров кремнезема $(HO)_3SiCH_2NHC(S)NHCH_3$ с одной молекулой воды методами квантовой химии (теория функционала плотности, метод B3LYP / 6-31G (d, p)). Были получены значения полной энергии переходного состояния с одной молекулой воды и энергии активации тион-тиольного таутомерного перехода для различных конформаций системы. Результаты этих расчетов показали, что в присутствии матрицы кремнезема активационный барьер уменьшается. В изученных системах он выше, чем в аналогичных системах в вакууме.

ВПЛИВ ПОВЕРХНІ КРЕМНЕЗЕМУ НА ТІОН-ТІОЛЬНУ ТАУТОМЕРІЮ ПРИЩЕПЛЕНИХ ГРУП ТІОСЕЧОВИНИ

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Було досліджено тіон-тіольну таутомерію в присутності молекул води груп тіосечовини, прищеплених на поверхні діоксиду кремнію. Конфігурація перехідного стану була розрахована шляхом моделювання молекули N, N-диметілтіосечовини в формах $(CH_3)_2(NH_2)_2CS$ / $CH_3NHCSHNCH_3$ і фрагмента кластерів кремнезему $(HO)_3SiCH_2NHC(S)NHCH_3$ з однією молекулою води методами квантової-хімії (теорія функціоналу густини, метод B3LYP / 6-31G (d, p)). Було отримано значення повної енергії перехідного стану з однією молекулою води і енергії активації тіон-тіольного таутомерного переходу для різних конформацій системи. Результати цих розрахунків показали, що в присутності матриці кремнезему бар'єр активації зменшується. У вивчених системах він вищий, ніж в аналогічних системах у вакуумі.