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STRUCTURE AND REDOX PROPERTIES OF HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE (RDX) AND OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX) ADSORBED ON A SILICA SURFACE. A DFT M05 COMPUTATIONAL STUDY

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Abstract

Adsorption of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) on (001) surface of α-quartz was studied at the M05/tzvp level using cluster approximation. Hydrogen bonds between nitramines and silica surface were analyzed by atoms in molecules (AIM) method. Electron attachment causes significant change in geometry of adsorbed complexes. Redox properties of adsorbed RDX and HMX were compared with those of gas-phase and hydrated species by calculation of the ionization potential, electron affinity, oxidation and reduction Gibbs free energies, oxidation and reduction potentials. Calculations show that adsorbed RDX and HMX have lower ability to undergo redox transformations than hydrated ones.

Keywords: silica, RDX, HMX, adsorption, reduction, oxidation.

СТРУКТУРА І ОКИСЛЮВАЛЬНО-ВІДНОВНІ ВЛАСТИВОСТІ ГЕСКАГІДРО-1,3,5-ТРИНІТРО-1,3,5-ТРИАЗИНА (RDX) І ОКТАГІДРО-1,3,5,7-ТЕТРАНІТРО-1,3,5,7-ТЕТРАЗОЦИНА (HMX) АДСОРБОВАНИХ НА ПОВЕРХНІ КРЕМНЕЗЕМУ. ТФГ M05 РОЗРАХУНКОВЕ ДОСЛІДЖЕННЯ

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Анотація

Вивчено адсорбцію гексагідро-1,3,5-тринітро-1,3,5-триазина (RDX) і октагідроциклоокта-1,3,5,7-тетранітро-1,3,5,7-тетразоцина (HMX) на (001) поверхні альфа-кварцу методом M05/tzvp з використанням кластерного наближення. Методом «атоми в молекулі» (AIM) проаналізовано водневі зв'язки між нітроамінами і поверхнею кремнезему. Приєднання електрону викликає значні зміни в геометрії адсорбованих комплексів. Проведено порівняльний аналіз окисно-відновних властивостей RDX і HMX у газовій фазі, у водному розчині та у адсорбованому стані. Розраховані потенціали іонізації, спорідненість до електрона, вільні енергії Гіббса процесів окислення і відновлення, потенціали окислення і відновлення. Розрахунки показують, що адсорбовані RDX і HMX мають більш низьку здатність зазнавати окислювально-відновних перетворень, ніж гідратовані.

Ключові слова: силіцій (IV) оксид, RDX, HMX, адсорбція, відновлення, окислення.

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СТРУКТУРА И ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ СВОЙСТВА ГЕКСАГИДРО-1,3,5-ТРИНИТРО-1,3,5-ТРИАЗИНА (RDX) И ОКТАГИДРО-1,3,5,7-ТЕТРАНИТРО-1,3,5,7-ТЕТРАЗОЦИНА (HMX) АДСОРБИРОВАННЫХ НА ПОВЕРХНОСТИ КРЕМНЕЗЕМА. ТФП M05 РАСЧЕТНОЕ ИССЛЕДОВАНИЕ

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Аннотация

Изучена адсорбция гексагидро-1,3,5-тринитро-1,3,5-триазина (RDX) и октагидроциклоокта-1,3,5,7-тетранитро-1,3,5,7-тетразоцина (HMX) на (001) поверхности альфа-кварца методом M05/tzvp с использованием кластерного приближения. Методом «атомы в молекуле» (AIM) проанализированы водородные связи между нитроаминами и поверхностью кремнезема. Присоединение электрона вызывает значительные изменения в геометрии адсорбированных комплексов. Проведен сравнительный анализ окислительно-восстановительных свойств RDX и HMX в газовой фазе, в водном растворе и в адсорбированном состоянии. Рассчитаны потенциалы ионизации, сродство к электрону, свободные энергии Гиббса процессов окисления и восстановления, потенциалы окисления и восстановления. Расчеты показывают, что адсорбированные RDX и HMX имеют более низкую способность подвергаться окислительно-восстановительным превращениям, чем гидратированные.

Ключевые слова: оксид кремния (IV), RDX, HMX, адсорбция, восстановление, окисление.

Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are well-known water and soil contaminants [1]. Their extensive use causes serious environmental problems due to toxicity of the nitramines. In the past decade many efforts were direct to remove these contaminants from polluted environments. Alkaline hydrolysis, photolysis, reduction by nanoscale zero-valent iron, oxidation by Fenton reagent and permanganate were found to be the most efficient methods [2–4]. An important information for development of remediation strategies is persistence of contaminants in natural environments, depended from ability to form stable complexes during sorption by soil and/or good aqueous solubility. Adsorption limits the potential for these compounds to migrate to groundwater.

Several studies to elucidate the adsorption of RDX and HMX by different components of soil were conducted [5–8]. It was found that the nitramines has a higher tendency to adsorb on the mineral phases than on organic matter. Adsorbed compounds undergo subsequent decomposition mostly through redox processes, thus it is very important to predict their ability to undergo reduction and oxidation transformations in adsorbed form. The objective of the present study is prediction of redox properties for RDX and HMX adsorbed on a silica surface, taken here as the (001) surface of α-quartz and comparison them with the same properties for dissolved in water nitramines.

Recently study of oxidative and reductive properties of trinitrotoluene, 2,4-dinitrotoluene, 4-dinitroanisole, and 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one, 5-amino-3-nitro-1H-1,2,4-triazole, and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane adsorbed to silica surfacewas conducted [9–11]. It was found that adsorbed nitrocompounds arehardier to transform by oxidation or reduction than their dissolved in watercounterparts. In this study, we extended investigation of redox properties of nitrocompounds under different environmental conditions to RDX and HMX.

Computational Methodology

The Gaussian 09 program package was used for all of the calculations [12]. To simulate the hydroxylated (001) surface for α-quartz a cluster approach was utilized. The dangling bonds of the cluster were saturated by hydrogen atoms in order to keep the silica model electroneutral. The models obtained contain three oxygen-silicon-oxygen layers, with a formula of $Si_{21}O_{62}H_{40}$. The geometry of all species was optimized at the M05/tzvp level. The harmonic vibrational frequencies were calculated for all structures obtained to establish that a minimum was observed. Solvent effects were taking into account by single-point calculations using the PCM(Pauling) and SMD solvation models for ion-radical and neutral molecule computations, respectively.

The Multiwfn program [13] was used to conduct a topological analysis of the distribution function of the electron density ρ(*r*) in the framework of the R. Bader *atoms in molecules* (AIM) theory.

The binding energy of interactions (E) was calculated with the Espinosa formula $E = 0.5V$, where V is the density of potential energy in a critical point. The energy of adsorption presents a difference between the total energy of the adsorbed complex and the energy of the separated silica and nitramine. Deformation energy of the silica surface $E_{def.}(S)$ presents a difference in energies of the silica surface model at the geometry optimized with the adsorbate after removing the contribution brought by nitramine and optimized silica surface model. Deformation energy of nitramine was calculated as a difference in energy of nitramine frozen within the geometry of the adsorbed complex and the energy of optimized nitramine. Adiabatic electron affinities (E_A) and ionization potentials (I_p) were computed as the total energy difference between the charged species and the neutral forms, corrected for zero point energy.

The Gibbs free energies of electron attachment and electron loss for adsorbed and dissolved in water nitramine were calculated as follows:

i) α-quartz adsorption:

$$\Delta G^0_{red,ads} = \Delta G^0(R^{-\cdot}_{ads}) - \Delta G^0(O_{ads})$$

$$\Delta G^0_{ox,ads} = \Delta G^0(O^{+\cdot}_{ads}) - \Delta G^0(R_{ads})$$

ii) water hydration:

$$\Delta G^0_{red,solv} = \Delta G^0(R^{-\cdot}_{solv}) - \Delta G^0(O_{solv})$$

$$\Delta G^0_{ox,solv} = \Delta G^0(O^{+\cdot}_{solv}) - \Delta G^0(R_{solv})$$

where, R and O denote reduced and oxidized species, respectively.

The values of the oxidation and reduction potentials are calculated as follows:

$$E^0_{red} = -\frac{\Delta G^0_{red}}{nF} + E_H \qquad E^0_{ox} = \frac{\Delta G^0_{ox}}{nF} + E_H$$

The absolute potential of the normal hydrogen electrode E_H was taken as –4.36 eV [14].

Results and Discussion

Adsorbed complexes

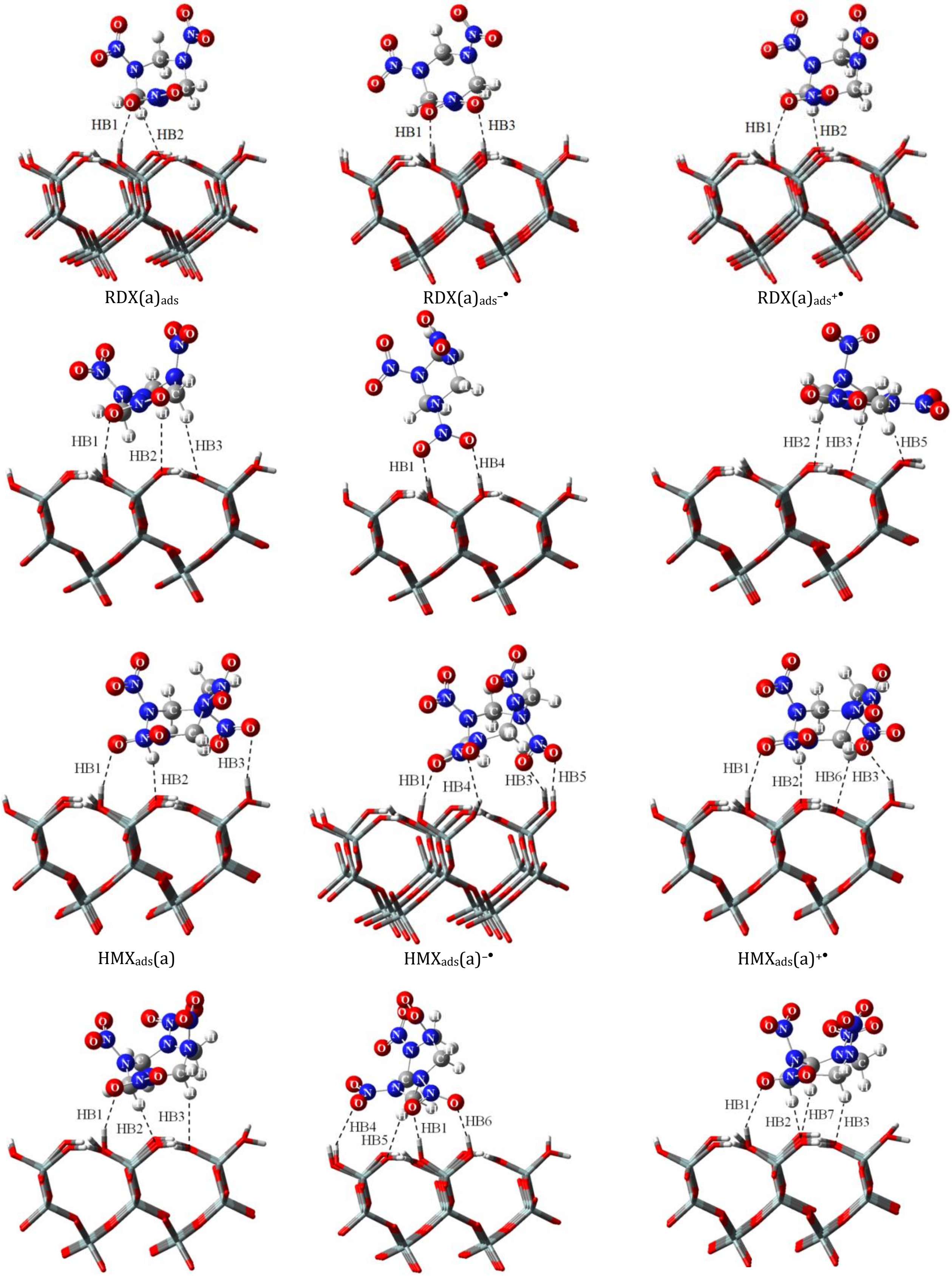
Nitramines RDX and HMX have different conformations. The most representative conformations, according to literature data [15, 16], were checked for ability to form stable complexes with silica surface. It should be noted that on the base of the preliminary calculation two stable complexes for RDX and two for HMX were chosen for further analysis (Fig. 1, Table 1). For clarity only hydrogen atoms on the top of the silica surface models are shown in the Fig. 1. Complexes RDX(a) and RDX(b) contain AAA and AAE conformations of RDX, respectively. Complexes HMX(a) and HMX(b) corresponds to boat-chair and α conformations of HMX (Fig. S1, SI). Calculated adsorption energy of RDX and HMX is in a range of –13.64 - –15.38 kcal/mol (Table 1). HMX is slightly better adsorbed on silica surface than RDX. Nitramines bind with silica surface by hydrogen bonds formed between the oxygen atoms of nitro-groups and the hydrogen atoms of the surface hydroxyl groups, and between the oxygen atoms of the surface and the hydrogens of the adsorbed nitramines (Fig. 1, Table 2).

An analysis of the data presented in Fig. 1 shows that total orientation of nitramines relative to the silica surface changes slightly after losing an electron while the changes are significant in case of electron attaching. Ionization also affects the amounts and strength of hydrogen bonds. As expected, in anion-radicals electronegative nitro-group orient close to the silica surface as compared with neutral ones, an amount of bonds between oxygens of nitrogroups and hydrogens of the surface is increase, the strength of (N–)O···H–O bonds increases. While in cation-radicals nitrogroups tend to stay away from the surface, (N–)O···H–O bonds length increase, their strength decrease. Instead, hydrogens of nitramines are placed close to the surface, and strength of C–H···O bonds increases. Ionization causes an increase of adsorption energy (Table 1). This means that ionized nitramines stronger bind to silica surface than the neutral ones. Calculated deformation energy for neutral complexes of silica surface is larger than that of nitramines (Table 1). This points a more significant modification of geometry of surface hydroxyl groups than geometry change of nitramines during adsorption (Fig. 1).

Table 1

M05/tzvp calculated adsorption energies (ΔE_{ads}), deformation energies of the silica surface ($E_{def.}(S)$) and adsorbed RDX ($E_{def.}$(RDX)), HMX ($E_{def.}$(HMX)) for complexes RDX$_{ads}$, HMX$_{ads}$, their anion- and cation-radicals, (kcal/mol)

Structure	ΔE_{ads}	$E_{def.}$(RDX)	$E_{def.}$(S)	Structure	ΔE_{ads}	$E_{def.}$(HMX)	$E_{def.}$(S)
RDX(a)$_{ads}$	–13.64	0.30	–0.53	HMX(a)$_{ads}$	–15.38	1.06	1.13
RDX(a)$_{ads}{}^{-\bullet}$	–40.77	–1.39	9.00	HMX(a)$_{ads}{}^{-\bullet}$	–21.91	7.15	8.66
RDX(a)$_{ads}{}^{+\bullet}$	–29.94	5.35	–0.18	HMX(a)$_{ads}{}^{+\bullet}$	–27.75	9.77	0.65
RDX(b)$_{ads}$	–14.20	0.21	–0.81	HMX(b)$_{ads}$	–14.66	0.50	1.47
RDX(b)$_{ads}{}^{-\bullet}$	–36.61	3.95	7.15	HMX(b)$_{ads}{}^{-\bullet}$	–37.76	1.57	12.71
RDX(b)$_{ads}{}^{+\bullet}$	–41.43	–1.35	1.56	HMX(b)$_{ads}{}^{+\bullet}$	–29.14	4.86	2.78



RDX(a)$_{ads}$ RDX(a)$_{ads}^{-\bullet}$ RDX(a)$_{ads}^{+\bullet}$

HMX$_{ads}$(a) HMX$_{ads}$(a)$^{-\bullet}$ HMX$_{ads}$(a)$^{+\bullet}$

HMX$_{ads}$(b) HMX$_{ads}$(b)$^{-\bullet}$ HMX$_{ads}$(b)$^{+\bullet}$

Fig. 1. The optimized structures of RDX and HMX adsorbed on a model of the (001) α-quartz surface and intermolecular H-bonds.

Table 2

M05/tzvp calculated geometrical characteristics of adsorbate-adsorbent H-bonds including H···Y, X···Y distances (Å) and X-H···Y angles (degree) for adsorbed RDX$_{ads}$, HMX$_{ads}$, their anion- and cation-radicals.

Bond	Bond type	RDX(a)$_{ads}$			RDX(a)$_{ads}^{-\bullet}$			RDX(a)$_{ads}^{+\bullet}$		
		X···H	X···Y	XHY	X···H	X···Y	XHY	X···H	X···Y	XHY
HB1	(N–)O···H–O	1.95	2.84	152.6	1.62	2.60	166.0	2.27	3.02	133.8
HB2	C–H···O	2.39	3.41	155.1	–	–	–	2.25	3.30	159.6
HB3	(N–)O···H–O	–	–	–	1.79	2.75	165.4	–	–	–
		RDX(b)$_{ads}$			RDX(b)$_{ads}^{-\bullet}$			RDX(b)$_{ads}^{+\bullet}$		
HB1	(N–)O···H–O	1.92	2.83	156.5	1.59	2.59	175.9	–	–	–
HB2	C–H···O	2.56	3.55	151.8	–	–	–	2.21	3.20	148.8
HB3	C–H···O	2.65	3.70	162.5	–	–	–	2.45	3.52	166.9
HB4	(N-)O···H–O	–	–	–	1.79	2.75	169.1	–	–	–
HB5	C–H···O	–	–	–	–	–	–	1.83	2.97	169.8
		HMX(a)$_{ads}$			HMX(a)$_{ads}^{-\bullet}$			HMX(a)$_{ads}^{+\bullet}$		
HB1	(N–)O···H–O	2.00	2.87	150.1	1.99	2.88	151.5	2.17	2.98	140.6
HB2	C–H···O	2.26	3.33	166.1	–	–	–	2.30	3.35	162.7
HB3	(N–)O···H–O	2.13	2.99	149.1	1.96	2.86	154.3	2.12	2.99	149.2
HB4	(N–)O···H–O	–	–	–	2.29	2.91	122.1	–	–	–
HB5	(N–)O···H–O	–	–	–	1.78	2.73	167.2	–	–	–
HB6	C–H···O	–	–	–	–	–	–	2.62	3.30	120.1
		HMX(b)$_{ads}$			HMX(b)$_{ads}^{-\bullet}$			HMX(b)$_{ads}^{+\bullet}$		
HB1	(N–)O···H–O	1.94	2.84	154.6	1.61	2.60	166.4	2.37	3.11	133.7
HB2	C–H···O	2.41	3.49	169.5	–	–	–	2.34	3.39	162.1
HB3	C–H···O	2.53	3.51	149.1	–	–	–	2.37	3.35	149.3
HB4	(N–)O···H–O	–	–	–	2.33	3.18	147.6	–	–	–
HB5	C–H···O	–	–	–	2.22	3.16	144.7	–	–	–
HB6	(N–)O···H–O	–	–	–	1.84	2.78	161.8	–	–	–
HB7	C–H···O	–	–	–	–	–	–	2.32	3.38	162.4

Electron attachment process causes increase of deformation energy for nitramines and for silica surface (Table 1). While effect of electron detachment is less significant.

The topological analysis of the electron density in the studied complexes shows the presence of intermolecular bond critical points (BCPs) between the hydrogens of C–H group and the closest oxygen atoms of the surface C–H···O, and between the oxygen of nitro-group and the closest hydrogen atoms of the surface O···H–O (Tables 3, 4). There is an exponential correlation between H-bonds lengths and electron density at BCPs with a correlation coefficient of 0.96 (Fig. S2, SI).

Table 3

Topological parameters for adsorbed RDX$_{ads}$, its anion- and cation-radicals

Bond	Bond type	ρ, $e\cdot$Å^{-3}	$\nabla^2\rho$, $e\cdot$Å^{-5}	H, au	E, kcal/mol
RDX$_{ads}$(a)					
HB1	(N–)O···H–O	0.0216	0.0887	0.0023	–5.52
HB2	C–H···O	0.0108	0.0397	0.0020	–1.85
RDX$_{ads}^{-\bullet}$(a)					
HB1	(N–)O···H–O	0.0551	0.1361	–0.0127	–18.67
HB3	(N–)O···H–O	0.0320	0.1020	–0.0015	–8.97
RDX$_{ads}^{+\bullet}$(a)					
HB1	(N–)O···H–O	0.0180	0.0783	0.0029	–4.33
HB2	C–H···O	0.0119	0.0433	0.0021	–2.04
RDX$_{ads}$(b)					
HB1	(N–)O···H–O	0.0236	0.0932	0.0017	–6.21
HB2	C–H···O	0.0074	0.0271	0.0014	–1.22
HB3	C–H···O	0.0061	0.0214	0.0011	–0.97
RDX$_{ads}^{-\bullet}$(b)					
HB1	(N–)O···H–O	0.0579	0.1370	–0.0144	–19.80
HB4	(N–)O···H–O	0.0349	0.1113	–0.0025	–10.32
RDX$_{ads}^{+\bullet}$(b)					
HB2	C–H···O	0.0150	0.0587	0.0026	–2.95
HB3	C–H···O	0.0092	0.0338	0.0019	–1.48
HB5	C–H···O	0.0348	0.1022	–0.0014	–8.91

Table 4

Topological parameters for adsorbed $\mathrm{HMX_{ads}}$, its anion- and cation-radicals

bond	bond type	ρ, $e\cdot$Å^{-3}	$\nabla^2\rho$, $e\cdot$Å^{-5}	H, au	E, kcal/mol
$\mathrm{HMX_{ads}}$(a)					
HB1	(N–)O···H–O	0.0193	0.0813	0.0027	−4.71
HB2	C–H···O	0.0137	0.0512	0.0024	−2.51
HB3	(N–)O···H–O	0.0144	0.0639	0.0031	−3.11
$\mathrm{HMX_{ads}^{-\bullet}}$(a)					
HB1	(N–)O···H–O	0.0198	0.0780	0.0024	−4.61
HB3	(N–)O···H–O	0.0238	0.0874	0.0014	−5.99
HB4	(N–)O···H–O	0.0127	0.0592	0.0030	−2.76
HB5	(N–)O···H–O	0.0345	0.1124	−0.0023	−10.29
$\mathrm{HMX_{ads}^{+\bullet}}$(a)					
HB1	(N–)O···H–O	0.0127	0.0586	0.0030	−2.70
HB2	C–H···O	0.0126	0.0477	0.0023	−2.29
HB3	(N–)O···H–O	0.0148	0.0646	0.0030	−3.17
HB6	C–H···O	0.0074	0.0286	0.0015	−1.32
$\mathrm{HMX_{ads}}$(b)					
HB1	(N–)O···H–O	0.0225	0.0900	0.0020	−5.80
HB2	C–H···O	0.0106	0.0374	0.0018	−1.79
HB3	C–H···O	0.0079	0.0015	0.0289	−1.35
$\mathrm{HMX_{ads}^{-\bullet}}$(b)					
HB1	(N–)O···H–O	0.0557	0.1326	−0.0132	−18.70
HB4	(N–)O···H–O	0.0085	0.0382	0.0024	−1.51
HB5	C–H···O	0.0146	0.0616	0.0028	−3.11
HB6	(N–)O···H–O	0.0309	0.1017	−0.0010	−8.57
$\mathrm{HMX_{ads}^{+\bullet}}$(b)					
HB1	(N–)O···H–O	0.0083	0.0388	0.0024	−1.57
HB2	C–H···O	0.0122	0.0441	0.0021	−2.16
HB3	C–H···O	0.0114	0.0429	0.0021	−2.04
HB7	C–H···O	0.0119	0.0452	0.0023	−2.13

Good correlation with a correlation coefficient of 0.99 was also observed between an interaction energy and an electron density at BCPs (Fig. S3, SI).

The calculated electron density properties of studied complexes show that the interactions between nitroamines and surface have low electron density ρ and positive Laplacian ($\nabla^2\rho > 0$) (Tables 3, 4). These values indicate that C–H···O and (N–)O···H–O contacts may be classified as closed-shell interactions. The electronic charge of the interactions is concentrated towards nucleus and is depleted in the internuclear region. Positive electron energy density values ($H > 0$) indicate noncovalent interactions, while negative H values mean that these interactions are partly covalent. Binding energy of interactions calculated with the Espinosa formula ranges from −1.22 kcal/mol for C–H···O bond to −19.80 kcal/mol for (N–)O···H–O bond. Energy values show that electron attachment causes an increase of hydrogen bonds strength between the nitramines and the surface. While an attachment of electron leads to decrease binding by H-bonds, except the case of RDX(b).

Redox properties

The calculated electron affinity, Gibbs free energy of reduction, and reduction potential characterize the ability of nitramines to be reduced (Table 5), while the ionization energy, Gibbs free energy of oxidation, and oxidation potential reflect the ability of nitramines to be oxidized (Table 6). Close values of Gibbs free energy of reduction and electron affinity, and, respectively, Gibbs free energies of oxidation and ionization energies indicate insignificant contribution of entropy $T\Delta S$ term in Gibbs free energy of redox transformation. Analysis of Tables 5 and 6 shows that redox properties depend on conformation of RDX and HMX.

Gibbs free energies of reduction or oxidation for adsorbed and solvated forms differ from gas-phase Gibbs free energy by contribution of adsorption and hydration, which are listed in Table 7. Calculated data show that hydration more decrease gas-phase energy than adsorption. This means that hydration more facilitates redox transformation of nitramines than adsorption. Indeed, as one can see from Tables 5 and 6, hydrated nitramines have larger reduction potentials and smaller oxidation potentials than adsorbed species.

Table 5

Electron affinities, Gibbs free energies of reduction, and reduction potentials of RDX and HMX calculated at the M05/tzvp and SMD/PCM(Pauling)/M05/tzvp levels.

Species	E_A, eV			ΔG^0_{red}, eV			E^0_{red}, eV	
	gas	ads	water	gas	ads	water	ads	water
RDX(a)	−0.87	−2.05	−3.22	−0.88	−1.97	−3.26	−2.39	−1.10
RDX(b)	−1.01	−1.98	−3.31	−1.04	−2.05	−3.25	−2.31	−1.11
HMX(a)	−1.84	−2.12	−3.64	−2.00	−1.97	−3.73	−2.39	−0.63
HMX(b)	−0.97	−1.97	−2.49	−1.05	−1.84	−2.36	−2.53	−2.00

Table 6

Ionization energies, Gibbs free energies of oxidation, and oxidation potentials of RDX and HMX calculated at the M05/tzvp and SMD/PCM(Pauling)/M05/tzvp levels

Species	I_p, eV			ΔG^0_{ox}, eV			E^0_{ox}, eV	
	gas	ads	water	gas	ads	water	ads	water
RDX(a)	9.89	9.18	6.92	9.86	9.15	6.90	4.79	2.54
RDX(b)	9.95	8.77	6.87	9.94	8.80	6.92	4.44	2.56
HMX(a)	9.65	9.11	6.38	9.64	9.04	6.39	4.68	2.03
HMX(b)	9.76	9.13	6.70	9.74	9.13	6.73	4.77	2.37

Table 7

Gibbs free energy components (eV) in case of the reduction and oxidation calculated at the M05/tzvp and SMD/PCM(Pauling)/M05/tzvp levels

Species	$\Delta\Delta G^0_{red,ads}$	$\Delta\Delta G^0_{red,solv}$	$\Delta\Delta G^0_{ox,ads}$	$\Delta\Delta G^0_{ox,solv}$
RDX(a)	−1.09	−2.38	−0.71	−2.96
RDX(b)	−1.01	−2.21	−1.14	−3.02
HMX(a)	0.03	−1.73	−0.60	−3.25
HMX(b)	−0.79	−1.31	−0.61	−3.01

Conclusions

Geometries of complexes formed by RDX and HMX on (001) surface of α-quartz were modeled at M05/tzvp level. RDX and HMX form C–H···O and (N–)O···H–O hydrogen bonds with surface. According to topological analysis of electron density these H-bonds may be classified as noncovalent and partly covalent closed-shell interactions. Electron attachment leads to increase binding between nitramines and silica surface due to stronger hydrogen bonds formation. Calculated data show that hydration more decrease gas-phase Gibbs free energies of reduction and oxidation than adsorption. Calculation of ionization potential, electron affinity, oxidation and reduction potentials show that adsorbed RDX and HMX are more resistant to oxidation and reduction processes as compared with the hydrated species.

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