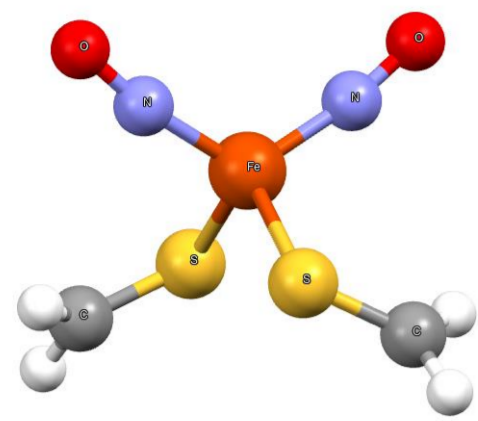


Abstract

The mechanisms of decomposition of a model dinitrosyl iron complex (DNIC) $\text{Fe}(\text{NO})_2(\text{SCH}_2)_2^+$ (1) in water have been studied using the density functional theory and polarizable continuum water model. Quantum chemical calculations employed the TPSSH and M06 functionals and def2-TZVP basis set. Reaction paths of water molecule attack at the DNIC considered were explored in aqueous medium. Hydrolysis of the thioformaldehyde ligand is found to be an exothermic process with a small activation energy, whereas exchange of $\text{NO}\cdot$ for H_2O is thermodynamically unfavorable. The calculations have predicted lower activation barrier for the associative mechanism with concerted replacement of SCH_2 by H_2O than for dissociative mechanism with homolytic bond cleavage of the Fe-S coordination bond in water. Inclusion of dispersion correction in TPSSH have brought the reaction energies from the considered functionals closer to each other for intermediates with strained crowded structure. In addition, the data of this work have shown importance of inclusion of solvent effect in the DFT calculations of molecular structures and reaction energies.

**Methods of calculations**

The electronic and molecular structures have been calculated using the hybrid meta-GGA functionals TPSSH and M06, and the triple-zeta valence basis set def2-TZVP. The DFT calculations of reactive species with unpaired electron employed unrestricted open-shell wave functions. The solvent effects were considered using the implicit polarizable continuum model PCM-SMD of water. The total electronic energy $E_{\text{el,w}}$ includes the intramolecular term and the free energy of electrostatic interactions of solute electron density with the polarizable continuum. The calculated Gibbs free energy of molecules in water G_w includes $E_{\text{el,w}}$ and the free-energy thermal contribution $G_{\text{therm,w}}$. The $G_{\text{therm,w}}$ term was obtained using harmonic approximation and contains translational, rotational, and vibrational parts. The reaction free energies in water $\Delta G_{\text{r,w}}$ included concentration corrections $\Delta G_{\text{r,conc}}$ for changing the standard state of 1 atm (in Gaussian-09) to the standard state in solution of 55.5 Mol for water molecule and 1 Mol for other reacting species. For the calculations we used program Gaussian-09.

Results

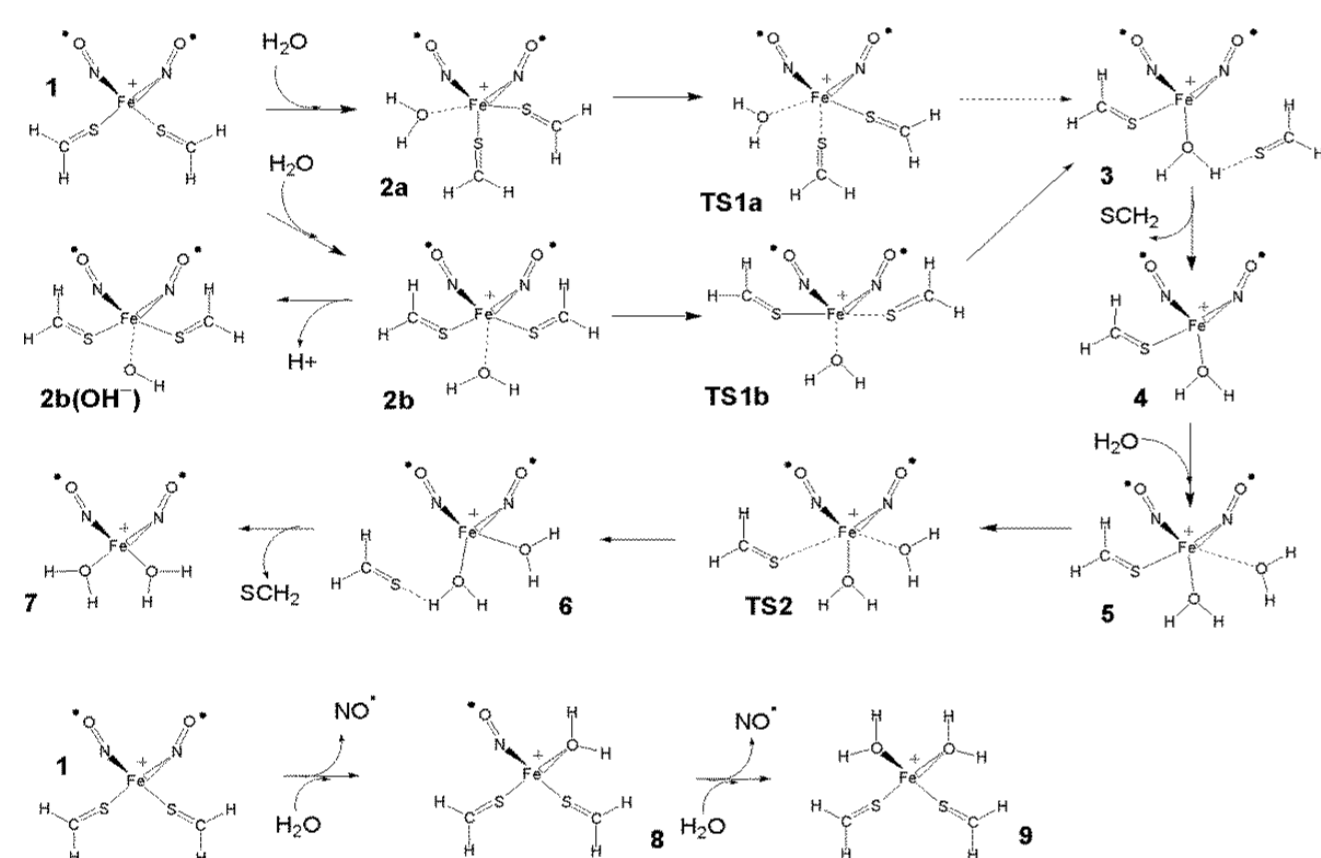
The iron-sulfur-nitrosyl complexes (ISNC) are actively studied compounds due to their applications as NO carriers and donors [1]. The chemical reactivity of these complexes is to a large extent determined by interplay of the thio and NO ligands at iron center. The thio ligands in ISNC are in many cases readily detached from coordinated metal. For instance, exchange reactions of thio ligands are observed in solution. In this work we consider anaerobic hydrolysis of a model DNIC with a small prototypic ligand thioformaldehyde which is a well-recognized ligand in metal complexes.

In the calculations, the multiplicity of DNIC 1 equaled two and the Fe atom in 1 was considered in the oxidation state (I) like in a related thiourea complex $\text{Fe}(\text{NO})_2(\text{SC}(\text{NH}_2)_2)^+$. The results of the DFT calculations predict that the lowest-energy conformation of 1 in water has the 3D structure similar to that of the D_{2d} conformer of the quaternary ammonium ion $\text{N}^+(\text{C}_2\text{H}_5)_4$. The potential energy barriers for rotations of thiocarbonyl ligands are less than $4 \text{ kJ}\cdot\text{mol}^{-1}$ that indicates labile structure of this coordination compound.

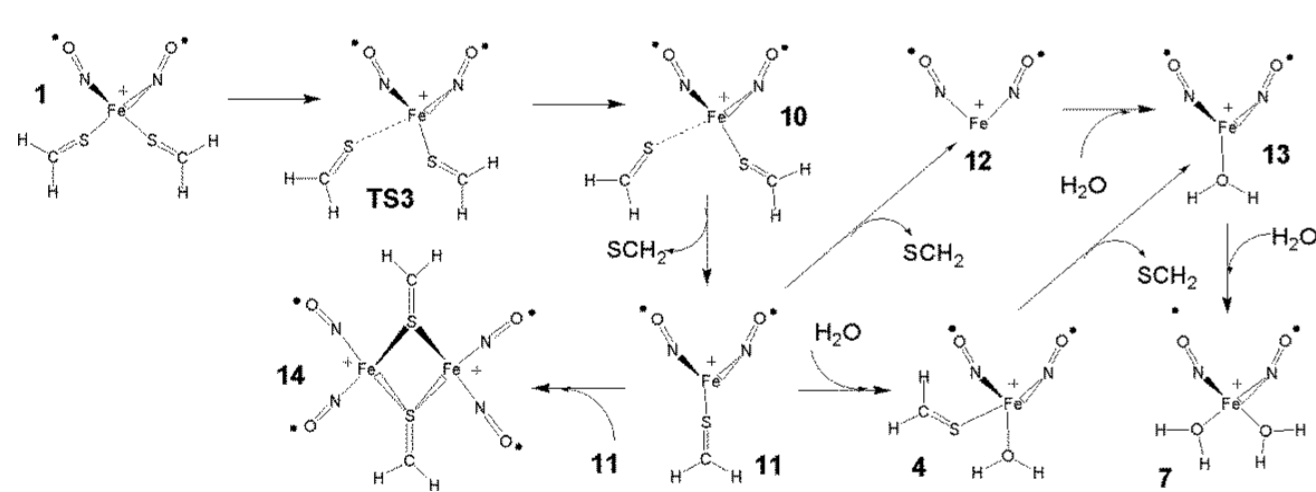
The calculated energies and optimized structures of reactive species along the reaction paths considered are shown below.

Table. Cumulative relative energies ($\text{kJ}\cdot\text{mol}^{-1}$) in water along the reaction paths at Schemes 1, 2. The energies of the products at the reaction steps are given relative to the sum of energies of DNIC 1 and two H_2O .

Reaction intermediates	$\Delta E_{\text{el,w}}$		$\Delta E_{0,w}$		$\Delta G_{298,w}$		$\Delta G_{\text{r,w}}$	
	TPSSH	M06	TPSSH	M06	TPSSH	M06	TPSSH	M06
1 + 2H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2a + H ₂ O	-10.3	-33.4	-3.8	-23.2	33.1	20.6	15.1	2.7
2b + H ₂ O	-23.1	-43.4	-14.4	-33.1	29.7	10.8	11.8	-7.1
TS1a + H ₂ O	-9.0	-28.7	-2.9	-20.4	39.8	23.6	21.9	5.7
TS1b + H ₂ O	-16.8	-35.7	-10.0	-28.5	34.8	13.7	16.8	-4.2
3 + H ₂ O	-35.5	-49.2	-27.7	-35.7	12.5	10.0	-5.4	-7.9
4 + SCH ₂ + H ₂ O	-22.0	-28.1	-19.7	-25.2	-20.2	-23.4	-27.2	-30.4
5 + SCH ₂	-28.0	-50.9	-17.7	-38.3	18.3	-2.9	-9.6	-30.8
TS2 + SCH ₂	-22.6	-51.0	-14.0	-38.8	24.9	-2.1	-3.9	-29.9
6 + SCH ₂	-42.6	-61.9	-32.9	-48.3	1.4	-11.3	-26.6	-39.1
7 + 2SCH ₂	-30.4	-43.1	-28.4	-37.6	-40.1	-50.4	-60.1	-70.3
8 + NO· + H ₂ O	24.5	25.7	24.9	33.7	26.4	37.7	16.4	27.8
9 + 2NO·	85.6	120.8	84.2	120.7	76.4	111.8	56.5	91.9
TS3 + 2H ₂ O	36.2	24.5	26.1	23.2	26.0	27.2	26.0	27.2
10 + 2H ₂ O	19.7	10.3	13.4	8.0	10.9	10.8	10.9	10.8
11 + SCH ₂ + 2H ₂ O	24.2	26.1	15.9	19.0	-23.1	-23.4	-15.1	-15.5
12 + 2SCH ₂ + 2H ₂ O	47.0	55.0	29.1	38.5	-55.8	-49.9	-39.9	-34.1
13 + 2SCH ₂ + H ₂ O	4.9	6.1	-1.9	3.2	-49.1	-42.3	-51.2	-44.9
14	30.6	63.4	35.5	64.5	26.1	51.3	34.1	59.2

Hydrolysis paths of DNIC 1 in water

Scheme 1. The associative route of the thio ligand hydrolysis and the products of NO substitution for complex 1.



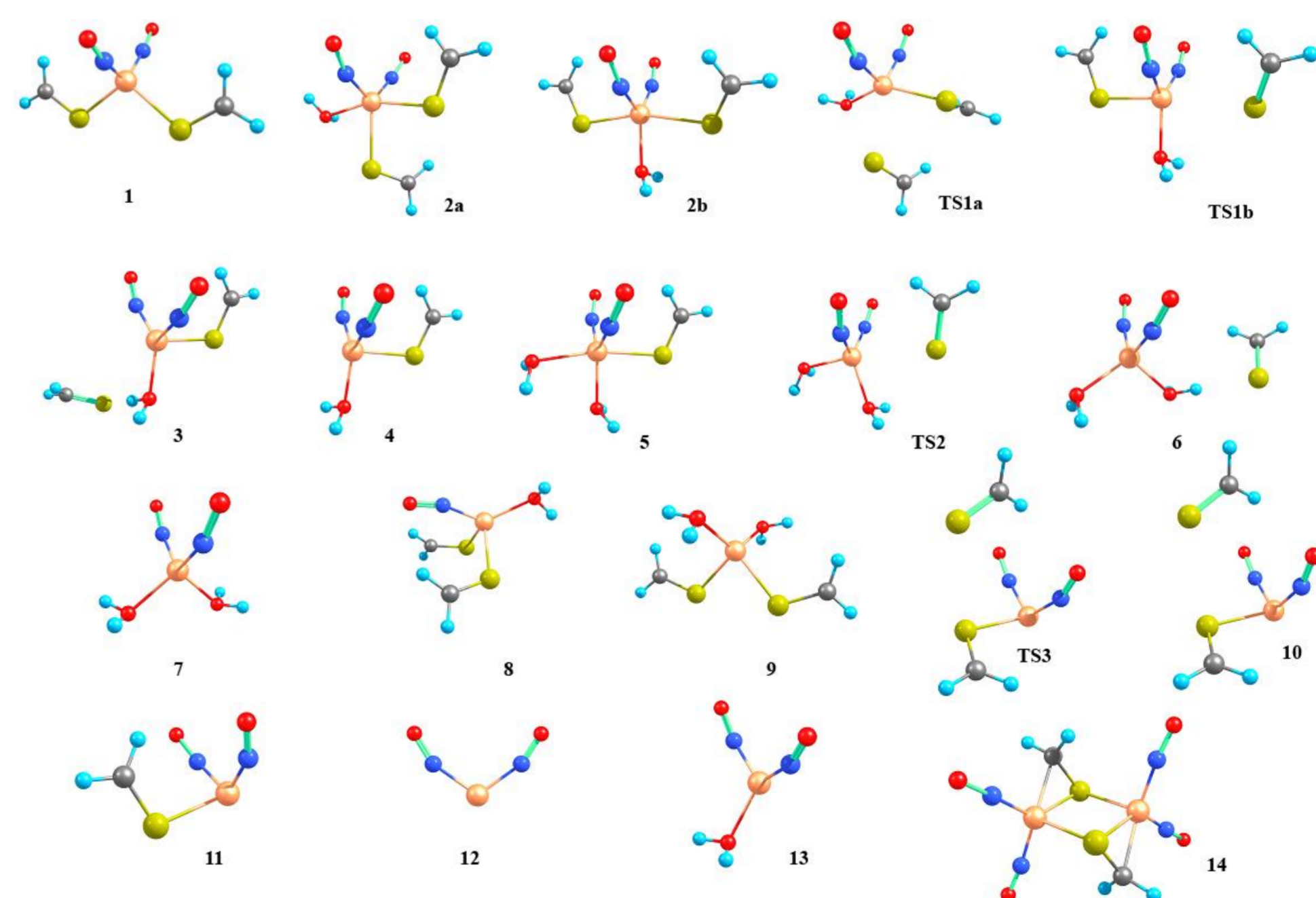
Scheme 2. The dissociative and dimerization routes of thioformaldehyde ligand hydrolysis.

Conclusions

In this work we have studied hydrolysis of cationic DNIC with a small thioformaldehyde ligand. The study of this model complex can provide useful insights into reactivity of the known DNIC [1] with larger thiocarbonyl ligands. It is found that hydrolysis of the thio ligand in $\text{Fe}(\text{NO})_2(\text{SCH}_2)_2^+$ is an exothermic process with a small activation energy, whereas exchange of NO by H_2O is thermodynamically not favorable in the absence of molecular oxygen [2]. The calculations show preference of the concerted exchange of thioformaldehyde for water via associative mechanism in comparison with the homolytic bond cleavage of the Fe-S bond via dissociative mechanism in water. Exchange of the first SCH_2 ligand for H_2O is rate determining in associative mechanism. A possible dimerization of the intermediate $\text{Fe}(\text{NO})_2(\text{SCH}_2)^+$ complexes in dissociative mechanism is unfavorable by several tens $\text{kJ}\cdot\text{mol}^{-1}$.

The calculations show a difference of $\sim 10 \pm 20 \text{ kJ}\cdot\text{mol}^{-1}$ between the relative electronic energies from the TPSSH and M06 calculations for the penta-coordinated reaction intermediates with strained crowded structure. Additional calculations, where we included dispersion correction to the TPSSH results, have brought the reaction energies for the functionals considered closer to each other. Despite the drawback in the treatment of non-covalent term, TPSSH in a better way reproduces experiment bond lengths and gives more compact structures for DNIC 1 than M06. In addition, this work has showed strong influence of water medium on molecular structures and reaction energies and importance of inclusion of solvent effect in the SCF calculations.

The number of ligands at the central iron changes in reactions of Schemes 1, 2 between two to five. The geometries of the complexes include tetrahedral, trigonal pyramid, triangular, or trigonal bipyramid shapes (Schemes 1, 2). The optimized geometries of the complexes with four-coordinated Fe(I) correspond to a regular tetrahedron in 1 and 7 or to a trigonal pyramid in 4. It is interesting to note that even in the structures 11 and 13 with three ligands the spatial orientations of Fe-S and Fe-N bonds correspond to tetrahedral configuration, i.e. no planar triangular structures are found around iron center with three ligands. The Mulliken spin densities and electron distribution for the c4 structure of 1 in water roughly correspond to the $\{\text{Fe}(\text{NO})_2\}^9$ configuration in Enemark-Feltham notation for metal nitrosyl complexes. The iron in DNICs is assumed to be in Fe(I) or Fe(III) oxidation states. The results of this work show that iron in DNIC 1 is of Fe(I) type and DNIC 1 keeps tetrahedral structure in water medium.



Optimized structures of reactants in the reaction paths from the TPSSH/def2-TZVP calculations in water

References

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