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Abstract.

Mechanism off the hydrogen atom abstraction from H_2S by triplet CrO_3, MoO_3 and WO_3. †

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Abstract: We have investigated mechanism off the hydrogen atom abstraction from H2S by triplet CrO_3, MoO_3 and WO_3 by quantum chemical ub3lyp/lanl2dz method. Activation energy of the CrO_3 + H_2S, MoO_3+H_2S, WO_3+H_2S reactions were calculated as: 2.45 kcal/mol, 2.41 kcal/mol, 2.16 kcal/mol. These values were greater than in the corresponding ones in the singlet state. Beside we have investigated the spin density distribution in the transition states all them calculated. Allocated spin density has said about spin density transition from one oxygen centre to sulfur atom. Transition have been uncompleted (because value sulfur's spin density was equal 0.429, at the same time spin density on oxygen atom was of 0.631 in the case of the CrO_3 + H_2S reaction). Transition in the transition state has not led to great change in difference between HOMO and LUMO for all system studied. The mechanism of the reaction have been proposed.

Keywords: photochemistry; hydrogen sulfur; MoO_3; CrO_3; WO_3.

1. Introduction

Exhaust sulfur components in atmosphere lead bad ly influence to our life. Desulfurization is one of the most important task to avoid ecological risks.[1-3] An usual way of the diesel fuel desulfurization is hydrodesulfurization. This method requires big amount of energy for reaching high temperature and it has also to be realize in the presence of hydrogen. Alternative method is to use a photochemical reaction of oxidation agent such as polyoxometalates. It has advantages like low temperature, light energy, green technology nature, etc.

The goal of our article is a quantum chemistry research of the photooxidation mechanism of hydrogen sulfur with the triplet state polyoxometalates. Our main hypothesis is that the oxidation mechanism includes a step of a hydrogen atom abstraction from H_2S by metal oxides such as CrO_3, MoO_3, WO_3 in triplet state.

2. Methodological part

We used ub3lyp/lanl2dz quantum chemical method. For compare probability of reactions involved we have determined their activation energies. It has been calculated like a difference between full electron energy of a transition state with correction for the zero-point vibrations added and total energy of the initial product correction for the zero-point vibrations added. For assign initial condition molecule was done preliminary search conform to minimum.

3. Results and Discussion

We have shown geometries of the initiate and transition states for the reactions in Figure 1-3. The corresponding geometry parameters are shown in Table 1.

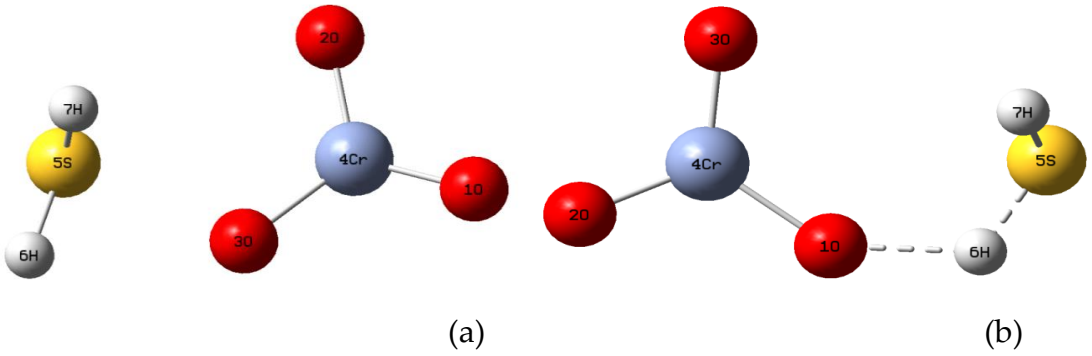


Figure 1. Geometries of the CrO_3+ H_2S reaction: (a) Initiate state; (b) Transition state.

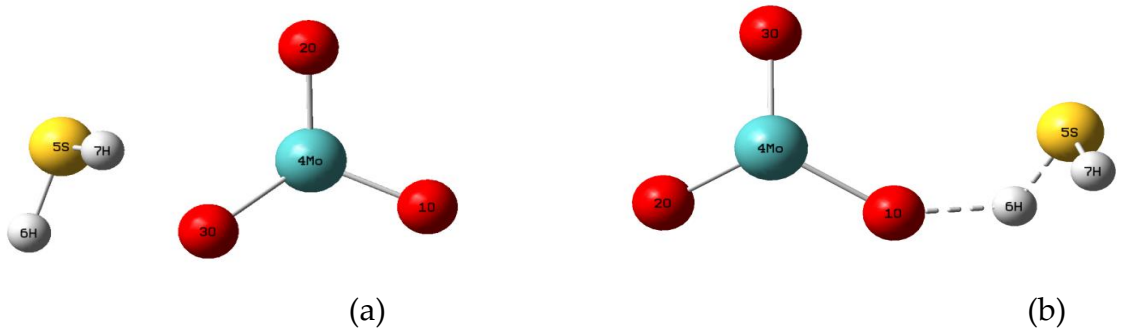


Figure 2. Geometries of the MoO_3+ H_2S reaction: (a) Initiate state; (b) Transition state.

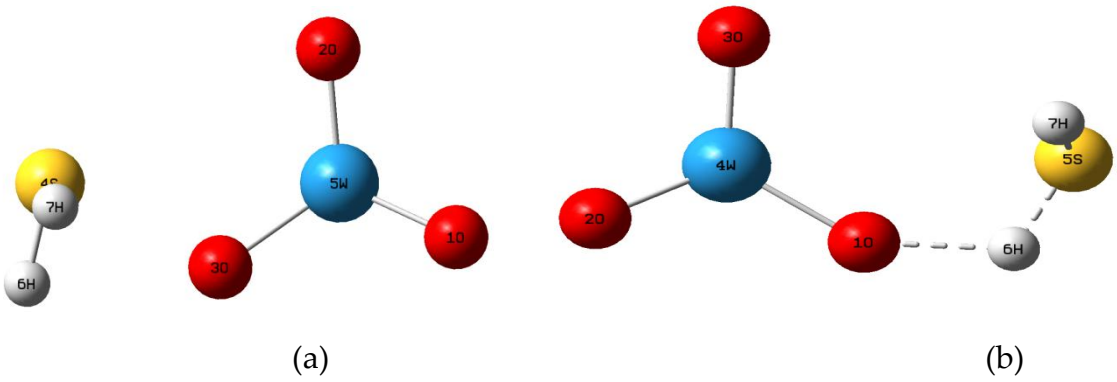


Figure 3. Geometries of the WO_3+ H_2S reaction: (a) Initiate state; (b) Transition state.

Table 1. The geometry parameters of the CrO_3 + H_2S, MoO_3+H_2S, WO_3+H_2S reactions systems.

Reaction	**Bond length Met-O, nm**		**Bond length O-H, nm**		**Bond length S-H, nm**		**Angle Met-O-H, degree**		**Angle S-H-O, degree**		**Dihedral angle Met-O-S, degree**	
	IS[1]	**TS[2]**	**IS**	**TS**	**IS**	**TS**	**IS**	**TS**	**IS**	**TS**	**IS**	**TS**
CrO_3 + H_2S	0.173	0.1738	0.271	0.171	0.137	0.140	104.58	145.73	64.02	116.91	112.12	118.82
MoO_3+ H_2S	0.188	0.1889	0.268	0.170	0.137	0.140	113.03	142.30	65.61	114.80	113.54	121.77
WO_3+H_2S	0.187	0.1871	0.269	0.170	0.137	0.140	120.91	149.36	66.34	114.62	118.42	120.78

[1]IS – initiate state; [2]TS – transition state

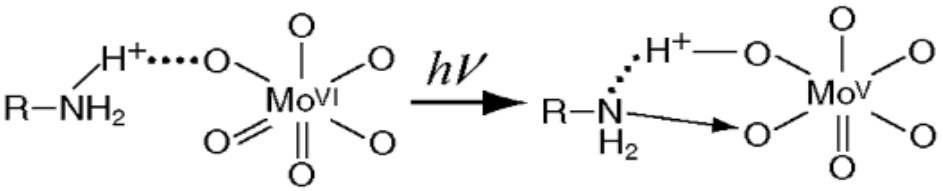
Table 1 has shown that there is large difference between the initiate and transition state in the O-H bond length, in the Met-O-H angle and the S-H-O angle values. One could note that (1) change has place near the reaction center, (2) there has place a transfer of hydrogen atom from H_2S to one of atom of $MetO_3$ in the triplet state.

Activation energy of these transfers are sufficiently small (See Table 2). The latter say that excitation of $MetO_3$ to the first singlet level and next intersystem crossing triplet state could increase probability of the oxidation. Usually suggest that reaction CrO_3 , MoO_3, WO_3 base on transfer electron density from atom O to atom Met. This mechanism is alternative to intersystem crossing.

Table 2. Activation energy of the $CrO_3 + H_2S$, MoO_3+H_2S, WO_3+H_2S reactions

Reaction	**E_a kcal mol^{-1}**
$CrO_3 + H_2S$	2.45
MoO_3+H_2S	2.41
WO_3+H_2S	2.16

One of mechanism was suggested with charge-transfer [4] and this shown on Scheme 1. Our study of electron density distribution seems to reveal that there is no appreciate change in electron density (see Table 3). Despite for Table 3 we can say about mechanism of the reaction as off hydrogen from atom S to atom O (see Figure 1-3).



Scheme 1. Mechanism of charge-transfer

Table 3. Electron density in the the $CrO_3 + H_2S$, MoO_3+H_2S, WO_3+H_2S reactions

CrO3		MoO3		WO3	
IS	TS	IS	TS	IS	TS
Cr 0.7984	Cr 0.8268	Mo 1.0261	Mo 1.0615	W 1.0857	W 1.1165
S 0.0355	S -0.0226	S 0.0248	S -0.0163	S 0.0525	S 0.0028
O - 0.3414	O -0.3275	O -0.4288	O -0.4183	O -0.4633	O -0.4518
O -0.3664	O -0.3401	O -0.4401	O -0.4179	O -0.4677	O -0.4585
O -0.4518	O -0.4910	O -0.5155	O -0.5613	O -0.5507	O -0.5804
H 0.1645	H 0.2099	H 0.1686	H 0.2120	H 0.1739	H 0.2219
H 0.1612	H 0.1445	H 0.1649	H 0.1404	H 0.1697	H 0.1496

One of important result has allocation spin density in intermediate table 4.

Table 4. Milliken atomic spin densities distribution

CrO3		**MoO3**		**WO3**	
IS	TS	IS	TS	IS	TS
1 O -0.0617	1 O -0.0522	3 O 0.6462	2 O 0.6072	1 O -0.0139	3 O -0.0029
2 O -0.0310	2 O -0.0274	2 O 0.0562	1 O 0.0720	2 O 0.0417	4 O 0.0428
3 O 0.6302	3 O 0.6130	1 O 0.0191	3 O 0.0150	3 O 0.5634	2 O 0.5449
4 Cr 1.0758	4 Cr 1.0701	4 Mo 0.8964	4 Mo 0.8998	4 S 0.4602	5 S 0.4759
5 S 0.4208	5 S 0.4293	5 S 0.4145	5 S 0.4391	5 H -0.0174	6 H -0.0155
6 H -0.0165	6 H -0.0151	6 H -0.0156	6 H -0.0151	6 H -0.0184	7 H -0.0194
7 H -0.0176	7 H -0.0176	7 H -0.0168	7 H -0.0180	7 W 0.9845	1 W 0.9742

There is allocation of spin density on metal atom Met, atom O, and atom S. So, we have proved our hypothesis about an advantage of hydrogen atom transfer between S and O atoms.

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