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Two Lower-barrier Channels in the Reaction of HF with HOBO

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Abstract: Two possible lower barrier reaction pathways in the reaction HF+HOBO $\longrightarrow$ H_2O+FBO are predicated by means of MP2 and CCSD(T) (single-point) methods. In the two channels, two stable intermediates are located, and thus, they are multi-step channels, which are more favorable in energy than direct single-step reaction pathway predicated by previous theoretical study. Therefore, the two pathways should be main reaction channels in experiments.

Keywords: *ab initio*, reaction channel, HOBO, FBO.

The reaction between HF and HOBO has attracted much attention because of the potential importance in the B/F/O/H combustion chemistry. Solid boron has long been recognized as an attractive alternative to conventional hydrocarbon-based fuels in aerospace systems[1-3]. But the formation of metastable species HBO and HOBO lead to the less energy release. Addition of fluorine to the system can effectively help to remove these metastable species by substantial energy release[3]. One of the possible reactions is:

$$HOBO + HF \longrightarrow FBO + H_2O \quad (1)$$

An *ab initio* computation has been performed by Linder and Page[4] to investigate the energy barrier of reaction (1). They predicated a planar transition state connecting the reactants and products with a 113.88 kJ/mol forward reaction barrier. Based on the structure of HOBO[5], we think that HF molecule is easy to add to –BO group. Therefore, we employed *ab initio* computation to restudy the mechanism of reaction (1), and two favorable reaction channels were found.

At MP2/6-311++G(d,p) level of theory, the geometric structures and parameters of additive intermediates (**I_1**,**I_2**), reactant HOBO+HF (**R**), product H_2O+FBO (**P**), and transition states are listed in **Figure 1**. In order to confirm whether the obtained transition states connect the right reactants and products, the intrinsic reaction coordinate (IRC) calculations are carried out at the MP2/6-311++G(d,p) level. All energies used in the paper are gained at the CCSD(T)/6-311++G(2d,2p)//MP2/6-311++G(d,p) level with zero-point energies inclusion. By means of these optimized species, a schematic

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potential energy surface is plotted in **Figure 2**. The relative energies of these species are also given in **Figure 2**. From **Figure 2**, we can easily know that there are three reaction channels from reactant HF+HOBO to products H_2O+FBO, and they include:

$$R \longrightarrow TS\ R/P \longrightarrow P \qquad (I)$$

$$R \longrightarrow TS\ R/I_2 \longrightarrow I_2 \longrightarrow TS\ P/I_2 \longrightarrow P \qquad (II)$$

$$R \longrightarrow TS\ R/I_1 \longrightarrow I_1 \longrightarrow TS\ I_1/I_2 \longrightarrow I_2 \longrightarrow TS\ P/I_2 \longrightarrow P \qquad (III)$$

The pathway (I) is a direct single-step process *via* transition **TSR/P** with a 118.39 kJ/mol forward barrier height. The process has been predicated by Linder and Page[4], and has a similar barrier height, 113.88 kJ/mol. But this is not the most favorable channel in energy, because the reaction barriers are 46.64 kJ/mol and 43.88 kJ/mol from reactant **R** to $\mathbf{I_2}$ and $\mathbf{I_1}$ in channels (II) and (III), respectively, which were completely ignored in the previous study[4]. And in view of the higher reverse barrier (256.06 kJ/mol for $\mathbf{I_2} \longrightarrow \mathbf{R}$ and 250.51 kJ/mol for $\mathbf{I_1} \longrightarrow \mathbf{R}$), we believe that pathways (II) and (III) are more favorable in energy than channel (I), and they should be main reaction pathways in experiments.

Figure 1 Predicated geometries at MP2/6-311++G(d,p) level of theory. (Bond lengths are in nanometers, and bond angles in degrees)

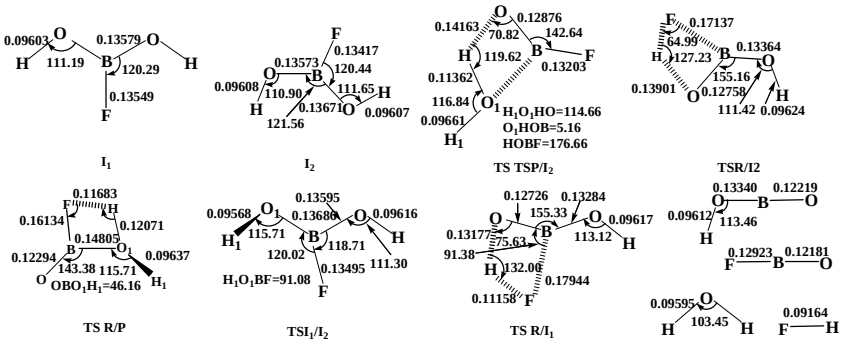
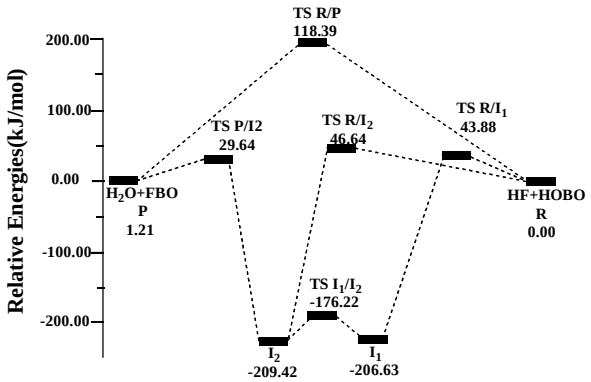


Figure 2 Schematic reaction pathways at CCSD(T)/6-311++G(2d,2p) //MP2/6-311++G(d,p) level of theory with zero-point vibrational energies inclusion.



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