

# Theoretical Study on the Reaction Mechanism of Formation of Lutidine Derivatives — Unexpected FLUORAL-P Compounds —

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**SUMMARY** The reaction path from acetyl acetone (pentane-2,4-dione) to lutidine derivative is calculated at the HF/3-21G + ZPC level (ZPC=zero point energy correction), and MP2/6-31G(d,p) + ZPC level. As a model for porous glass,  $H_2Si=O$  and  $(OH)_2Si=O$  make chemical bonds or strong complex with FLUORAL-P that decrease the activation energy of a  $H_2O$  elimination reaction.

**key words:** lutidine, reaction path, molecular orbital, porous glass

## 1. Introduction

The explicit detection of the concentration of the formaldehyde in the air becomes more and more important in these years, because the formaldehyde could be a reason of the sick building syndrome, sensory irritation of the eyes, nose, throat, and atopic dermatitis. Formaldehyde also has carcinogenicity and mutagenicity. The formaldehyde is contained in the building material, wallpaper, paint, domestic house ware [1]–[4]. WHO sets a guideline of indoor levels as 0.08 ppm. Therefore, how to measure the concentration of formaldehyde in the air within the building becomes very important.

The measurements of the formaldehyde usually use the acetyl acetone method (Nash Reagent) [5]. This reaction occurs in the aqueous solution and does not proceed in the gas-phase. The method utilizes the reaction of two acetyl acetone molecules, ammonium ion, and formaldehyde molecule yielding the lutidine derivative.

For the measurement in the gas-phase, we need to absorb the formaldehyde in aqueous solution. Finally, the identification of the concentration of the lutidine derivative is performed by the color strength of solution at 407 nm.

Maruo and co-workers showed  $\beta$  diketones and ammonium salts in nanoporous glass can be used instead of aqueous solution [6]. The color is changed as these depending on the concentrations of formaldehyde. There are several interesting features of the lutidine derivative in porous glass. In aqueous solution, the absorbance of the lutidine derivatives decreases after certain standing time, however, in porous glass, it does not in methyl phenyl case. (3,5-dibenzoyl-1,4-dihydro-2,6-dimethylpyridine).

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In dimethyl case, it is the same as in aqueous solution. 1,3-diphenyl-1,3-propanedione (phenyl-phenyl case) does not react in the aqueous solution but does in the porous glass and the absorption intensity decreases when increasing the amount of formaldehyde. Reasons for these are still mystery.

In this communication, as a first step of figuring out the environment effects, we perform ab initio molecular orbital calculations to obtain the reaction path from pentane-2,4-dione to the lutidine derivative. Based on the potential surface obtained, we also try to explain the difference of the environment (in aqueous solution or in porous glass) in one elementary reaction.

## 2. Method of Calculation

The calculations are performed at the HF/3-21G level for the optimization and the frequency calculations (HF/3-21G/HF/3-21G + ZPC) (ZPC=zero point energy correction), and at the MP2/6-31G(d,p) level for the optimization and the frequency calculations (MP2/6-31G(d,p)/MP2/6-31G(d,p) + ZPC). All the calculations are performed with Gaussian09 program package [7].

Model calculations for considering the difference of the environment (in aqueous solution or in porous glass) are also performed. The water is approximated by water molecule and the porous glass is approximated by  $H_2Si=O$  and  $(OH)_2Si=O$ .

## 3. Results and Discussion

Figure 1 shows a possible reaction path from acetyl acetone to lutidine derivative whose detail was discussed previously. Along with the reaction path of Fig. 1, we performed ab ini-

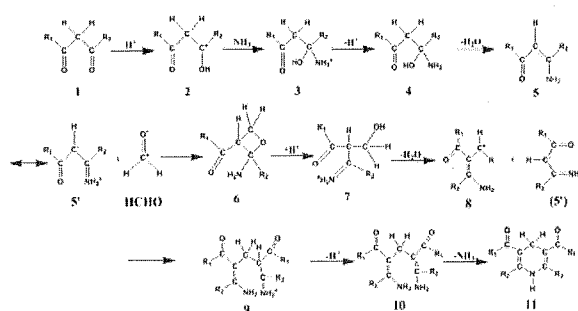


Fig. 1 Possible Reaction path from acetyl acetone to lutidine derivative.

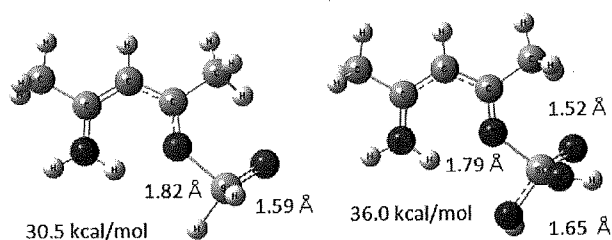


Fig. 2 Schematic view of  $\text{H}_2\text{Si}=\text{O}$  and  $(\text{OH})_2\text{Si}=\text{O}$  complex of FLUORAL-P.

tio molecular orbital calculations and here is a energy diagram. At the present time, the full reaction path is obtained at the MP2/6-31G(d,p) level only starting from pentane-2,4-dione.

The energies of addition and elimination of a proton are always problematic in this type calculation because the formation of a proton is not considered. The addition of a proton always gives huge stabilization energy, and the elimination of a proton gives huge destabilization energy.

We consider the effect of a proton is not so serious throughout this study. Among these elementary reactions, the largest energy barrier is the elimination of  $\text{NH}_3$  and formation of lutidine derivative. Second highest energy barrier corresponds to a reaction from **4** to **5** FLUORAL-P. The TS of **4** to **5** has the highest energy along the reaction path and we consider this elementary reaction is significantly important.

**4** is the initial state. At the transition state, OH and H make a water molecule and then elimination of this water molecule occur. We get a **5** that is FLUORAL-P. The energy barrier of this reaction is too high and the reaction does not proceed in gas-phase.

Therefore, we consider the effect of the environment. For models of porous glass, we simply considered a  $\text{H}_2\text{Si}=\text{O}$  and  $(\text{OH})_2\text{Si}=\text{O}$  and for a model of aqueous solution, one water molecule. We calculate the optimized structures of complexes between FLUORAL-P molecules, because these molecules are important intermediates of the reaction.

Very interestingly, Si atoms in this model make a chemical bond to oxygen atom as shown in Fig. 2. We confirmed the carbon analogue  $\text{H}_2\text{CO}$ , formaldehyde, of course, does not make a chemical bond. It is not so surprising, considering  $\text{SiO}_2$  makes a crystal but  $\text{CO}_2$  does not. However, we are not sure this is true or not. A water molecule makes hydrogen bonds as shown here.

About the reaction from **4** to **5** with  $\text{H}_2\text{Si}=\text{O}$ , the activation energy is about 42.9 kcal/mol at HF/3-21G level and 7.6 kcal/mol less than original reaction and 40.3 kcal/mol at MP2/6-31G(d,p) level, this is 7.2 kcal/mol less than original reaction.

In Table 1, the activation energies of the formation of FLUORAL-Ps. are summarized. MP2/6-31g(d,p) + ZPC is

Table 1 The barrier heights of the formation reaction of FLUORAL-P with various environment. All energies are in kcal/mol, and include ZPC.

	HF/3-21G	HF/6-31G(d,p)	MP2/6-31G(d,p)
Gas phase	50.5	58.4	47.5
$\text{H}_2\text{O}$	51.6	58.0	48.9
$\text{H}_2\text{SiO}$	42.9	54.8	40.0
$(\text{OH})_2\text{SiO}$	39.2	52.5	36.9
Gas Phase, $\text{R}_2=\text{Ph}$	51.9*	59.2	...
Gas Phase, $\text{R}_1=\text{R}_2=\text{Ph}$	67.4*	...	...

\*Not include ZPC

the most reliable. With introducing the porous glass model, the activation energy is greatly reduced from 47.5 kcal/mol to 36.9 kcal/mol, that is 10.6 kcal/mol, at MP2/6-31G(d,p) + ZPC.

At HF/6-31G(d,p) level, the activation energy is almost the same as gas phase. We don't know a reason why only at this level the energy is not changed. However, this is not the most reliable level of the theory. We also would like to note about the substituent effect. Introducing one phenyl-group does not change the activation energy, but introducing two phenyl-groups drastically increase the activation energy. This is a reason why  $\text{R}_1 = \text{phenyl}$  and  $\text{R}_2 = \text{phenyl}$  lutidine derivative does not yield in aqueous solution.

In summary, we have calculated the reaction path from acetyl acetone (pentane-2,4-dione) to lutidine derivative. As a model for porous glass,  $\text{H}_2\text{Si}=\text{O}$  and  $(\text{OH})_2\text{Si}=\text{O}$  make chemical bonds or strong complex with FLUORAL-P that decrease the activation energy of a  $\text{H}_2\text{O}$  elimination reaction.

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