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## Computational reaction mechanism study of the elimination of 2-pentanone

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### ABSTRACT

Theoretical studies for reaction mechanism of the gas phase elimination of 2-pentanone were carried out at B3LYP/6-31+g(d) level of theory. The mechanism for elimination is Norrish type II. The elimination reaction proceeds via a six-membered cyclic transition state with the formation of ethylene and propen-2-ol (acetone enol), which rearranges to the ketone. The calculated kinetic and thermodynamic parameters are in reasonable agreement with the reported experimental values. Analysis of the progress along the reaction coordinate, in terms of geometrical parameters suggest these reactions are dominated by the abstraction of a hydrogen atom from the  $\gamma$ -carbon by the carbonyl oxygen to give the diradical, and together with an important cleavage of C $\alpha$ -C $\beta$  bond in the transition state through concerted reaction mechanism.

**Keywords:** 2-pentanone, Six-membered ring transition state, Density Functional Theory.

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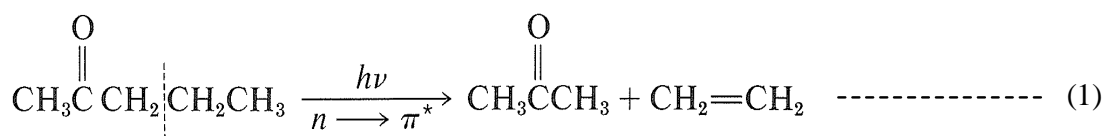
### INTRODUCTION

Ketones are a major class of organic chemicals and are widely used as solvents. They are important in the chemistry of the atmosphere and in combustion systems from direct emissions and as intermediates[1,2]. Their photodissociation in the lower atmosphere results in formation of free radicals and may influence the atmospheric oxidation capacity. Ketones are also used as fuel tracers for monitoring fuel properties, such as concentration, temperature, density, pressure, velocity, and distribution, using laser-induced fluorescence [1,2] and as fuel additives in reducing soot emissions [3,4].

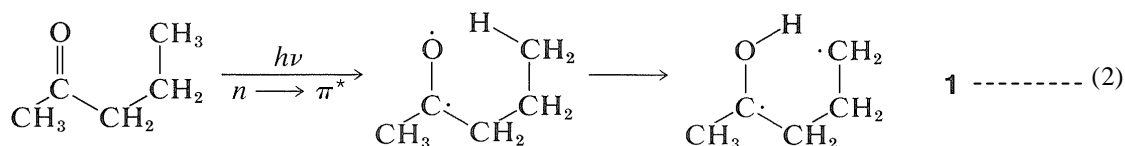
Chemical kinetics and dynamics of unimolecular reactions of isolated molecules in the gas phase are well understood [5,6]. The framework of a unimolecular process is often applied, at least as an idealization, to condensed phase processes although the effects of the environment on the process can be profound [7].

Photo induced hydrogen abstraction reaction, which is better known as the Norrish type II reaction, has been a highlight in the development of a general picture of how photochemical reactions occurs[8]. The rate constant for internal hydrogen abstraction depends on electronic configuration, on C-H bond strength or inductive substituent effects, and on conformational factors. These factors will determine the observed product ratios of photoreactions where more than one product is possible.

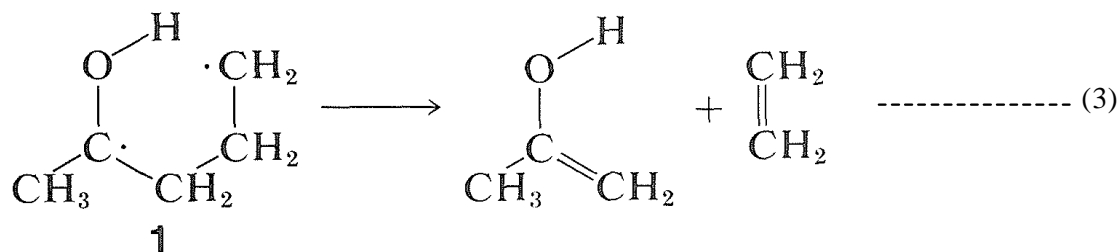
Carbonyl compounds are widespread in the atmosphere. Certain carbonyls are directly emitted by various sources, but the vast majority of them are produced in the atmosphere by oxidation of hydrocarbons [9]. Photolysis is an important removal pathway for atmospheric carbonyls. In the lower atmosphere, where the availability of radiation is limited to a wavelength of above 290 nm, the photolysis of carbonyls is driven by their weak absorption band in the wavelength range 240–360 nm as a result of a dipole forbidden  $n \rightarrow \pi^*$  transition [9,10]. Photolysis of Ketones, that have at least one  $\gamma$ -hydrogen on a chain connected to the carbonyl group such as pentanone, in this pathway (Norrish type II process), cleavage occurs at the  $C\alpha$ - $C\beta$  bond to give, as the major product, a ketone of shorter chain length and an alkene. Thus for 2-pentanone is known to occur through the following pathways in equation (1):



This reaction occurs in an interesting way. Whatever the nature of the  $n \rightarrow \pi^*$  excited state, S1 or T1, the primary photochemical reaction is the abstraction of a hydrogen atom from the  $\gamma$ -carbon by the carbonyl oxygen to give the diradical 1, as in equation (2):



The subsequent dark reactions readily are understood as typical of diradicals, cleavage of 1 at  $C\alpha$ - $C\beta$  gives ethene and an enol, as in equation (3).



A large number of gas-phase unimolecular reaction, which have been studied, appeared to take place by way of 4-centre and 6-centre cyclic activated complexes [11].

Serinyel et al [12]. for example, have published on the combustion kinetics of 3-pentanone and used thermochemistry and kinetic parameters corresponding to studies on acetone in their model development. Several studies on the fundamental thermochemistry of the intermediate radicals on ketones or their elementary oxidation kinetics have recently appeared. Sebbar et al.[13]. published on the thermochemistry of 2-butanone and show that although the primary C–H bond on butanone adjacent to the carbonyl is similar to acetone, the secondary C–H bond energy is more than 5 kcal mol<sup>-1</sup> weaker. Hudzik and Bozzelli [14] have also reported on thermochemical parameters of series of ketones as a function of temperature and reveal problems with matching entropy and heat capacity experimental data with vibration analysis using only frequencies from DFT and ab initio methods.

In this work, the mechanism of unimolecular elimination reaction of 2-pentanone to give ethene and enol will be discussed by means of the description of the energy, the geometry, and the stability of transition state structures involved in such reaction. This information provides a detailed energy profile for 2-pentanone elimination that matches conclusions which have been obtained experimentally.

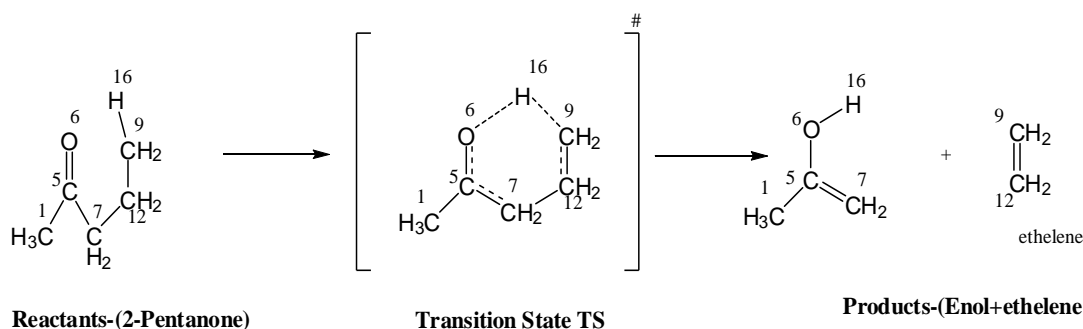
### METHOD OF CALCULATIONS

2-pentanone was chosen as model compound to study the mechanism of intramolecular elimination reaction. In the present study Density Functional Theory Study B3LYP (DFT) level of theory calculations were performed with the Gaussian09 [15] software packages, running in an Intel Pentium (R) 1.86 GB personal computer. All structures were fully optimized at the Density Functional Study (DFT) level, using the high level 6-31+g(d) basis set in gas phase. Also, the geometries of the reactants, products, intermediates, and transition states involved in the reactions were all fully optimized by using B3LYP/6-31+g(d). The structures thus obtained were subjected to vibrational analysis calculations toward their characterization as local minima (all positive force constants) or transition states (one imaginary force constant only). For the later structures, IRC[16] calculations were performed along the transition vector defined by the vibration mode of this imaginary frequency in order to assess that the saddle point structure connected downhill the corresponding forward and backward minima. This methodology allowed the identification of the reaction intermediates and transition state structures along the reaction path. The standard state is 1 atm., which is the default in Gaussian calculations.

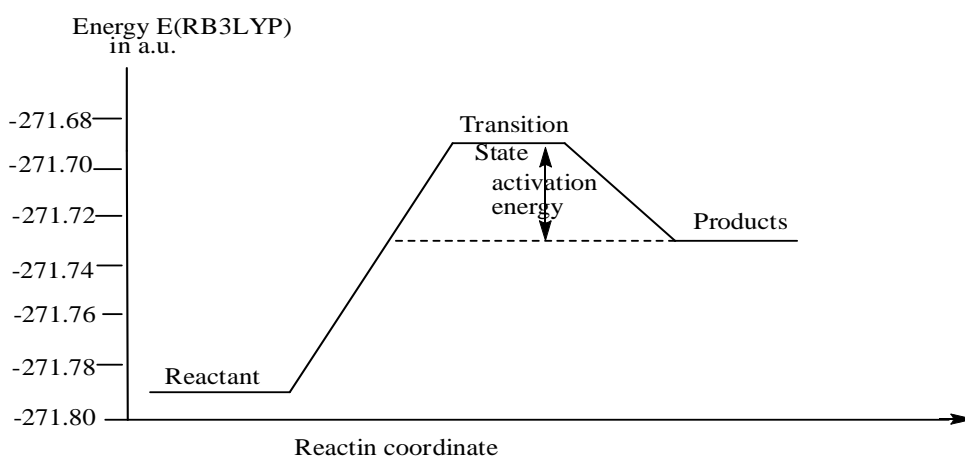
### RESULTS AND DISCUSSION

The elimination reaction of aliphatic ketones is kind of a Norrish type II reaction, which generally is the photochemical intramolecular abstraction of a  $\gamma$ -hydrogen by the carbonyl group to produce a 1,4-biradical as a primary photoproduct through cyclic transition state.

The mechanism of intramolecular elimination reaction of 2-pentanone to give ethene and enol (1-3 in scheme 1), scheme 1 shows the atoms directly involved in the reaction and the overall process. Figure 1 shows the energy profiles for the process in the gas phase with B3LYP/6-31+g(d). Tables 1 and 3 show the relative energies,  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  data for the structures involved, and table 2 show the bond length for each steps of the structures of the reaction path from reactants to products in Angstrom.



Scheme 1: Mechanism of Intramolecular elimination Reaction of 2-pentanone



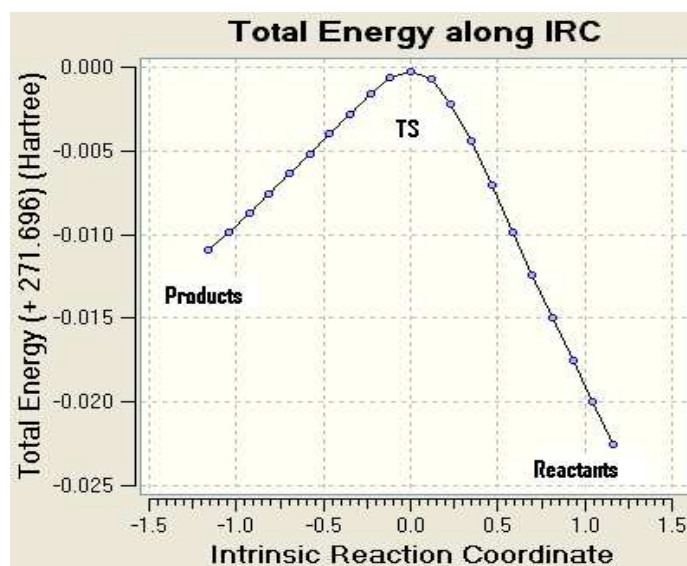
**Table 1. Energies (RB<sub>3</sub>LYP) for each of the structures of the reaction path from the standard thermochemistry output of a frequency calculation<sup>a</sup>**

| Structure              | ENERGY E(RB <sub>3</sub> LYP) |
|------------------------|-------------------------------|
| Reactants <sup>b</sup> | -271.7935                     |
| Transition state       | -271.6962                     |
| Products               | -271.7377                     |

<sup>a</sup>All structures were fully optimized. Cartesian coordinates of all structures are available as supplementary material. Energy in a.u.

<sup>b</sup>Reactants, cyclic transition state-TS, and product respectively (refer to Scheme 1).

**Six-member ring Transition state Formation:** The starting point for this step process is structure 1 (scheme 1) where the incoming carbonyl oxygen (O6) of 2-pentanone is the site of the nucleophilic attack, where the hydrogen atom (H16) abstracted from the  $\gamma$ -carbon by the carbonyl oxygen (O6). The distance H16-O6 is 3.30402 Å at the start (table 2, scheme 1), which shortened to 1.19210 Å in transition state, simultaneously the bond H16...C9 (1.09712 Å) in the reactant stretched to 1.42206 Å in the transition state, the bond C9...C12, which distance is 1.53370 Å is shortened to 1.40189 Å, partial formation of double bond (table 2), the carbonyl bond C5...O6 distance is 1.22013 Å, which stretched to 1.30932 Å i.e partial formation of sigma bond in the transition state, simultaneously there is a partial formation of the double between C7...C5, from 1.52423 Å to 1.38304 Å. The bond between C12...C7, starts to break from 1.54405 Å to 2.26644 Å in the transition state. This mechanism occurs via six-membered ring transition state TS. The calculated result of the vibrational analysis shows that there is only one strong imaginary frequency in the transition states, and the imaginary frequency of TS is  $-1320.38i$ . The vibration vector direction of corresponding imaginary frequency represents the fracture and generation of the molecular bond to construct the six-membered ring cyclic transition state. The transition state are verified by the intrinsic reaction coordinate (IRC) analysis, that is, TS connects directly the reactant and product in the reaction path, The reaction pathway includes only a one-step elementary reaction process, figure 2.



**Figure 2. Intrinsic Reaction Coordinate (IRC) analysis of six-membered ring transition state using B3LYP/6-31+g(d) methods**

The energy barriers for the elimination reaction of 2-pentanone to form six-membered ring transition state (TS) is  $56.13 \text{ kcal mol}^{-1}$  (table 3), downhill from these transition state structure, the system evolves to form products (scheme1) via the formation of an C9-C12 double bond and complete transfer of the (H16) to oxygen (O6), and complete breaking of C7-C12 bond to form ethylene and enol, scheme 1 and figure 3.

Table 2. Bond length for the structures of the reaction path from reactants to products in Angstrom

| Bond length in Å | Reactants | Transition state TS | Products |
|------------------|-----------|---------------------|----------|
| O6-H16,          | 3.30402   | 1.19210             | 0.97526  |
| H16...C9,        | 1.09712   | 1.42206             | 2.54581  |
| C9...C12,        | 1.53370   | 1.40189             | 1.33686  |
| C12...C7,        | 1.54405   | 2.26644             | 4.39922  |
| C7...C5,         | 1.52423   | 1.38304             | 1.34218  |
| C5...O6,         | 1.22013   | 1.30932             | 1.37134  |

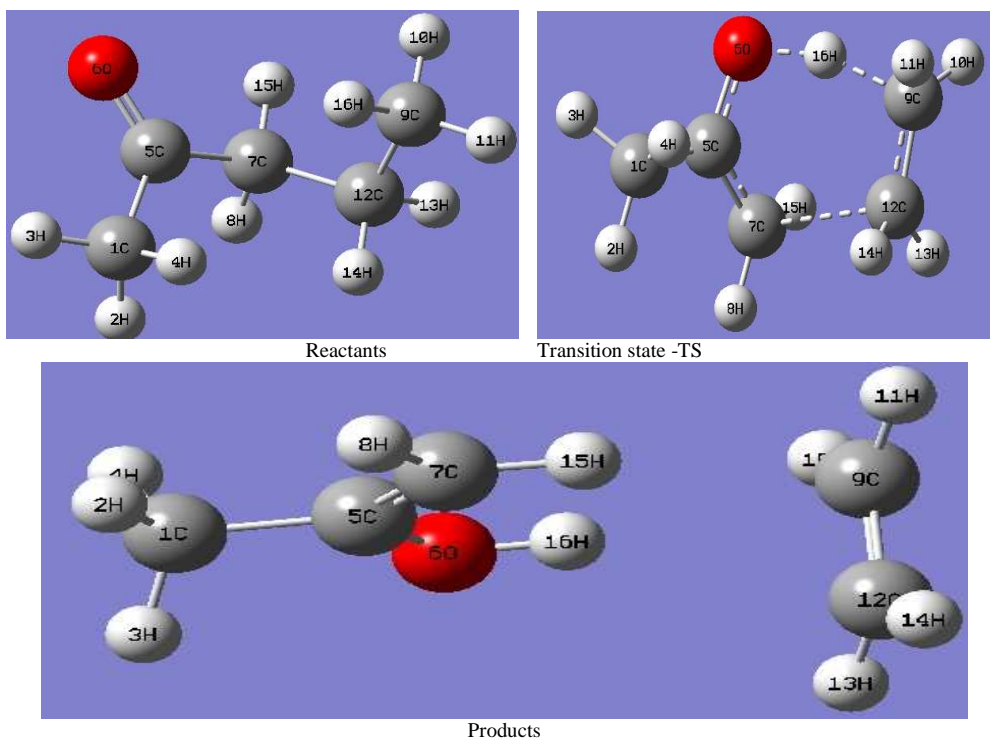


Figure 3. Optimized structures of reactants , six-membered ring transition state- TS, and products calculated by B3LYP/6-31+g(d)

According to the results obtained above in the energy profile for the elimination of 2-pentanone figure 1, and Intrinsic Reaction Coordinate (IRC) analysis figure 2, the reaction is endothermic.

Table 3: Calculated energies of reactants, six-membered ring transition states, and products using B3LYP/6-31+g(d) in kcal mol<sup>-1</sup><sup>a,b</sup> of elimination of 2-pentanone

| Compound               | $\Delta E$<br>kcal mol <sup>-1</sup> | $\Delta G$<br>kcal mol <sup>-1</sup> | $\Delta H$<br>kcal mol <sup>-1</sup> | $\Delta S$<br>Cal mol <sup>-1</sup> K <sup>-1</sup> |
|------------------------|--------------------------------------|--------------------------------------|--------------------------------------|-----------------------------------------------------|
| Reactants <sup>c</sup> | 0                                    | 0                                    | 0                                    | 0                                                   |
| Transition state       | 56.1313                              | 57.3474                              | 56.1307                              | -4.079                                              |
| Products               | 22.3554                              | 34.3049                              | 21.7624                              | 42.065                                              |

<sup>a</sup> All structures were fully optimized. Cartesian coordinates of all structures are available as supplementary material.

<sup>b</sup> Energies reported relative to the sum of energies of separated reactants.

<sup>c</sup> Reactants, cyclic transition state and product refer to Scheme 1.

If we consider the energy values (table 3) calculations (B3LYP) show that the initial elimination has energy barrier of 56.13 kcal mol<sup>-1</sup>, whereas the potential energy barrier to form the product is 22.35 kcal mol<sup>-1</sup>. This suggests that the elimination reaction of 2-pentanone is endothermic and one step process. Similar conclusions for this type of reaction have been drawn from the theoretical and experimental results for other simple ketones [17].

If Gibbs energy is considered, B3LYP calculations show barriers of 57.34 kcal mol<sup>-1</sup> for elimination of 2-pentanone to form six-membered ring transition state and 34.30 kcal mol<sup>-1</sup> to form the ethylene and enol.

### CONCLUSION

On the bases of our elimination model, carbonyl oxygen is main role in hydrogen transfer from  $\gamma$ -carbon to form biradical through six-membered ring transition state.

Intramolecular elimination of 2-pentanone take place by concerted reaction mechanism.

According to thermodynamic point of view the reaction is endothermic reaction.

### Supplementary Informations

Supplementary information (output results of B3LYP calculations) are available free of charge, on request.

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