The Theoretical Study of the Thermolysis of Acetylacetone*

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Abstract The thermal decomposition of acetylacetone has been studied with MINDO/3 MO theory. The results obtained show that the enol forms are more stable than the tone forms; the activation energies of the reaction (1) and (2) are 210.250 and 225.501 kJ·mol⁻¹, respectively.

Keywords: Acetylacetone, Thermolysis, MINDO/3 method, IRC pathway

Acetylacetone (AcAc) is known to include most of enol forms (76%) due to its relatively weak central C-H bonds as well as its effective intramolecular hydrogen bonding [1]. Choudhury and Lin have recently carried out a detailed pyrolytic study under wall-less genuinely homogeneous conditions using a shock tube in the temperature range of 1120-1660 K [2]. The reaction channels having lower activation energy in their hitherto unknown and possibly dominant ones are in the following way:

The results of their study suggested also that the reaction (3) for the production of

acetone and ketene [3] is not important under the condition used. Its thermal decomposition mechanism is not at all understood. In order to examine thermolysis mechanism of AcAc,

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we have studied these three reactions with MINCO/3 method. The results obtained is presented in this paper.

1 Computational Methods

The equilibrium geometries of the reactants and products are fully optimized by the energy gradient method. The structures of the transition states(TS) were optimized by Powell's method [4] and identified by the calculations of the vibrational analysis. For the pathways of the reaction (1)–(3), we have made a detailed analysis of the Intrinsic Reaction Coordinate (IRC) [5]. All the calculations were carried out with the standard MINDO/3 method [6] in the program GEOMOS [7].

2 Results and Discussions

2.1 The relative stability of the isomers of AcAc

AcAc has some enol form and tone form isomers, the most stable enol and tone form of it obtained by optimizing with the energy gradient method are the enol(2) and tone(1), respectively (to see Figure 1: b) and c)). The energy difference of the most stable enol and tone form $\Delta E (=E_{\text{enol}(2)} - E_{\text{tone}(1)})$ is equal to $-37.04\text{kJ}\cdot\text{mol}^{-1}$, this show that the enol form is more stable than the tone form, and that the calculative result is qualitatively consistent with the experimental result [1].

Fig.1 Geometrical structures:

a) enol(1); b) enol(2);

c) tone (1); d) tone(2)

Lengths in angstroms; angles in degrees.

Fig.2 Geometries of the products:

a) $\text{CH}_3\text{C}\equiv\text{CCOCH}_3$;

b) $\text{CH}_2\text{CCHCOCH}_3$ c) H_2O ;

d) $(\text{CH}_3)_2\text{C}=\text{O}$; e) CH_2CO

2.2 Thermolysis of AcAc(enol)

Starting with the enol(1) and enol (2) that are the most favourable configurations for the reaction (1) and (2), respectively, the mechanism of the thermolysis of AcAc(enol) is studied. The geometries obtained by calculations of the products are shown in Figure 2: a), b) and c). The energy differences between the reactants and the products of the

reaction (1) and (2) are 78.630 and 147.114 kJ·mol⁻¹, respectively. If the energy difference of reaction is approximately taken to be the heat of reaction, these two values are compared with the experimental heat of reaction (83.680 and 163.176 kJ·mol⁻¹) [2]. The reaction (1) and (2) are all endothermal.

The preliminary geometry of the transition state (TS) has been searched along the minimum energy reaction pathway, then it was fully optimized using Powell's method. The geometries of TS1 (the transition state of the reaction (1)) and TS2 (the transition state of the reaction (2)) are shown in Figure 3: a) and b). It is observed from the Figure 3 that TS1 and TS2 have the four-centered structure.

The calculations of the vibrational analysis show that the eigenvectors of the imaginary vibrational modes of TS1 and TS2 connect with the reactants and products (be omitted), which confirm that TS1 and TS2 obtained by Powell's method are reliable. IRC pathways of the thermolysis of AcAc are shown in Figure 4: a) and b). The activation barriers of the reaction (1) and (2) are 210.250 (E_a^1) and 233.254 (E_a^2) kJ·mol⁻¹, respectively. E_a^1 is not equal to E_a^2 , and they are little lower than the experimental value 254.387 kJ·mol⁻¹ [2].

Fig.3 Geometries of TS: a) TS1;
b) TS2; c) TS3

Fig.4 IRC pathways: a) reaction(1);
b) reaction(2); c) reaction(3)
The energy of the reactat is taken to
be zero. S is reaction coordinate.

2.3 The thermolysis of AcAc(tone)

AcAc(tone) is decomposed into CH_2CO and $(\text{CH}_3)_2\text{CO}$ according to the reaction (3). We have studied this reaction, starting with the most favourable configuration—tone(2). The geometries of the tone(2), $(\text{CH}_3)_2\text{CO}$ and CH_2CO are also shown in Figure 1: d), Figure 2: d) and e), respectively. The energy difference of the reaction (3) is equal to 44.622 kJ·mol⁻¹, so the reaction (3) is also endothermal. TS3 (the transition state of the reaction (3)) obtained is shown in Figure 3:c). IRC pathway of this reaction is shown in Figure 4: c). The activation barrier of the forward reaction E_a^3 is equal to 412.664 kJ·mol⁻¹, which suggests that the reaction (3) is not important in the temperature range of 1120–1660 K.

3 Conclusions

The results obtained by MINDO/3 MO method show that: (1) The enol forms of acetylacetone are more stable than the tautomer forms; (2) The activation barriers of the reaction(1), (2) and (3) are 210.250, 225.501 and 412.664 kJ·mol⁻¹, respectively, and the reaction(1) and (2) are the possibly dominant reaction channels in the thermolysis; (3) TS1 and TS2 have all the four-centered structures, which support the Choudhury and Lin's experimental results.

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乙酰丙酮热分解反应的理论研究

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摘要 用 MINDO/3 方法研究了乙酰丙酮的热分解反应. 研究结果表明, 醇式构型比酮式构型稳定; 具有最低能垒的两个反应通道——反应(1)和(2)的活化位垒分别为 210.250 和 225.501 kJ·mol⁻¹.

关键词: 乙酰丙酮, 热分解, MINDO/3 方法, 内禀反应坐标