

Kinetic Analysis of Acetone Combustion Reactions

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Abstract: Acetone is an important intermediate specie in several combustion mechanisms and is a potential candidate fuel. It is also a by-product in the biomass fermentation [1,2]. Hence it is crucial to develop a consistent kinetic mechanism of combustion of this biofuel, in order to better understand its process of combustion. A combustion mechanism has already been proposed by Sarathy et al [3]. In this context, this work aims to investigate some uni- e bimolecular reactions, which are of great importance to the initiation phase of the acetone combustion process, predict new kinetic parameters and then improve the former combustion mechanism. The reactions are: (R1) $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3 + \text{CH}_3\text{CO}$; (R2) $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{CO}$; (R3) $\text{CH}_3\text{COCH}_3 \rightarrow \text{H}_2 + \text{CH}_3\text{COCH}$; (R4) $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_2$; (R5) $\text{CH}_3\text{COCH}_3 + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{COCH}_2$. Therefore, calculations of geometry optimization, frequency and reaction paths have been performed at M06-2X/cc-pVDZ and M06-2X/aug-cc-pVTZ levels of calculation. Moreover, single points calculations have been performed at the CCSD(T)/aug-cc-pVTZ level. Rate coefficients of reactions R2 – R5 have been calculated by canonical transition state theory in a range of temperature of 500 – 2000 K. For reaction (R1), microcanonical rate coefficients (RRKM) have been calculated and the temperature and pressure dependence has been investigated through the solution of Master Equation, adopting the weak collision model. Rate coefficients have been determined in the range 500 – 2000 K and 10 – 38000 torr. Concerning the geometry optimizations, the improvement of the basis set quality did not yield significant differences on the bond lengths and angle values, except for the CH_3COCH specie, in which the $\text{C}_{(\text{CH})}\text{CO}$ angle decreases as the quality of the basis set increases. Barrier heights and reaction energy differences calculated at the DFT level with either DZ or TZ basis set are very close, exception is noted for (R4), in which the TZ result for the reaction energy difference is $4.7 \text{ kcal mol}^{-1}$ smaller than the DZ result. The single point calculations have also not significantly changed the former energy differences. The barrier heights determined at the CCSD(T)/aug-cc-pVTZ level were (in kcal mol^{-1}): 87.5 (R2), 102.2 (R3), 65.2 (R4) and 47.2 and 47.7 (R5). The larger deviation observed for the CCSD(T) and M06-2X barrier heights was $3.2 \text{ kcal mol}^{-1}$ (for reaction R4), and the mean value was $1.7 \text{ kcal mol}^{-1}$, indicating that the single point calculations have only slightly improved the results. All of these reactions were found to be endothermic, with CCSD(T)/ aug-cc-pVTZ reaction energy differences (in kcal mol^{-1}): 81.0 (R1), 21.7 (R2), 101.4 (R3), 12.0 (R4) and 47.2 (R5). For reaction (R1), Troe parameters have been estimate, with low pressure Arrhenius parameters of $8.34 \times 10^{-5} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $62.30 \text{ kcal mol}^{-1}$, high pressure of $6.54 \times 10^{17} \text{ s}^{-1}$ and $85.91 \text{ kcal mol}^{-1}$, and parameters P1,



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P2, P3 and P4 respectively: 1.05 , 3.29×10^{10} , 7.20×10^2 and 2.08×10^9 . This fit has shown an excellent agreement with some experimental results [4,5] and also provides reliable rate coefficients at higher pressures. For the other reactions, the Arrhenius expression at CCSD(T) level of calculation were (units: kcal mol^{-1} and s^{-1} or $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$): $k_2(T) = 4.43 \times 10^{13} \exp(-89.23/RT)$; $k_3(T) = 3.07 \times 10^{15} \exp(-106.16/RT)$; $k_4(T) = 3.89 \times 10^{13} \exp(-66.42/RT)$ and $k_5(T) = 1.82 \times 10^{-10} \exp(-52.56/RT)$. For the unimolecular reactions, the branching ratios have demonstrated that the reaction (R1) is the most important for temperature values above 1000 K, while for lower temperatures, reaction (R4) prevails. On the other hand, it is well known that the hydrogen abstraction by O_2 molecules is the dominant step in the initiation phase of low temperature combustion reactions (lower than 1000 K). Hence, a competition between the reactions (R4) and (R5) is expected. Ignition delay times have finally been calculated for the acetone combustion at high and low temperature regimes using the original mechanism [3]. Experimental results [6] obtained in the range from 1346 to 1633 K have compared to our predicted results. The calculated ignition delay times obtained from the original model [3] were higher than the experimental data [6] with an average error of 81%. After optimization of the combustion model (achieved by including our suggested kinetic parameters), the calculated errors are lower, decreasing to 24%. Therefore, in this work it has been shown that, for these reactions, our DFT calculations yields good molecular properties to be applied on chemical kinetics, comparable to high level *ab initio* calculations. Moreover, rate coefficients have been calculated, providing reliable and more accurate Arrhenius parameters for acetone combustion mechanism.

Key-words: Transition State Theory, Rate coefficients, Troe Parameters.

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