

Comparative Kinetic Analysis of Hydrogen Abstraction Reactions by OH Radicals: Dimethyl Ether and Diethyl Ether

Vinícius Nunes da Rocha, Glauco Favilla Bauerfeldt

Universidade Federal Rural do Rio de Janeiro, BR-465, Km 7 Seropédica, RJ

Abstract: Aliphatic ethers have been indicated as possible additives for fuels [1]. In its combustion mechanisms, the initiation is given from the unimolecular and bimolecular reactions, including reactions with OH radicals, which follow a hydrogen abstraction mechanism [2]. Concerning the Atmospheric Chemistry, OH radicals are the most important oxidants in troposphere, responsible for the chemical removal of the majority of the pollutant organic volatile compounds. This study aims at the theoretical description of the reactions of dimethyl ether (DME) and diethyl ether (DEE) with OH radicals, prediction of rate coefficients and kinetic parameters, and the comparative analysis on the results. The calculations have been performed at the M06-2X/aug-cc-pVTZ level, using the Gaussian09 program [3]. Canonical variational rate coefficients have been calculated with the kcvt program. These reactions have been previously discussed in the literature. Here, new stationary points have been located, as pre- and post-barrier complexes as well as new saddle points. The geometries of the intermediates and the corresponding saddle points keep some similarities, and their connections have been confirmed by intrinsic reaction coordinate (IRC) calculations. These calculations allowed the proposal of novel reaction channels. For DME, three pre-barrier complexes have been located at 0.76, 4.81 and 5.05 kcal mol⁻¹ below the isolated reactants and connected to their respective saddle points, lying at 0.29, -0.34 and 1.57 kcal mol⁻¹, respectively (the reported relative energy values include vibrational zero point energy corrections). In the DEE mechanism, two pre-barriers were located, stabilized at 1.40 and 6.12 kcal mol⁻¹ below the isolated reactants. These stationary points are connected to their saddle points, one of them at 2.40 kcal mol⁻¹ and three remaining at -0.20, -0.99 and -1.58 kcal mol⁻¹, respectively (concerning the isolated reagents and including zero point energy corrections). The global reactions are exothermic and products are predicted to lie at -22.44 kcal mol⁻¹ (CH₃OCH₂ + H₂O), -16.72 kcal mol⁻¹ (CH₃CH₂OCH₂CH₂ + H₂O) and -24.36 kcal mol⁻¹ (CH₃CH₂OCHCH₃ + H₂O), in good agreement with thermochemical predictions from literature values. This model is more detailed than the (best and most recent) mechanism proposal found in the literature [4]. Our predicted molecular properties and reaction paths have been used to predict rate coefficients in the range from 250 to 2000 K. Our predictions reveal an increasing behavior of the coefficients with the temperature in the DME mechanism and, in contrast, in the range from 250 to 400 K, a non-Arrhenius behavior is observed for the DEE + OH rate coefficients, confirming previous experimental results. Both respect the experimental values, as well as the chemical nature concerning the function of temperature. For the DME, the most recent expression for the



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rate coefficients found in the literature is $8.45 \times 10^{-18} (T^{2.07}) \exp(0.521/RT)$ [5] and our predicted rate coefficients are fit under the expression $1.10 \times 10^{-17} (T^{2.02}) \exp(0.596/RT)$. Small deviation among these values are noted. For DEE, Arrhenius parameters for this reaction are available in the literature only in the range from 250 to 400 K, suggesting a non-Arrhenius behavior in this range of temperatures [6]. This trend has not been observed in the most recent theoretical investigation on the kinetics of this reaction [7]. Our calculated rate coefficient, at 300 K, is $4.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas the experimental value, at this temperature, is $1.24 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As mentioned above, detailed reaction path calculations have been performed with the objectives of mapping the potential energy surface and collecting the required information for the prediction of accurate rate coefficients in a large temperature range. The good agreement between the kinetic parameters obtained from our proposed models and the experimental results allow the conclusion that the present mechanisms are consistent. Moreover, the temperature dependence of the rate coefficients for the OH + DME and DEE reactions have been here, for the first time, explained. Finally, our results represent new contributions to Combustion and Atmospheric Chemistry areas concerning the reactivity of aliphatic ethers.

Key-words: Diethyl Ether, Dimethyl Ether, Combustion Chemistry, Atmospheric Chemistry, OH Reactions.

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