Modeling the Reaction of $C_2H_5+O_2$

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Introduction

Modeling of low temperature ethane oxidation requires an accurate description of the reaction of $C_2H_5+O_2$, since its reaction channels either accelerate the oxidation process via chain branching, or inhibit it by forming stable less-reactive products. Before the discovery of the new concerted elimination channel[1], which is the direct formation of $C_2H_4+HO_2$ from ethylperoxy, the isomerization of ethylperoxy ($CH_3CH_2OO\bullet$) to hydroperoxyethyl ($C\bullet H_2CH_2OOH$) was considered the lowest energy channel. According to the Walker and Morley[2] scheme, subsequent reactions of hydroperoxyethyl lead to chain branching, thus promoting ignition. The new lower-lying concerted elimination path is significantly faster than the isomerization, reducing the importance of the isomerization channel and its subsequent chain-branching reactions.

Data are available on different aspects of the $C_2H_5+O_2$ system, for example, on the overall rate constant[3,4] of the reaction and on the production of ethylene[5,6], HO_2[7], and ethylene oxide[6]. Different groups have characterized this reaction theoretically. The latest theoretical studies by Miller et al.[8,9] and Sheng et al.[10], both of which incorporated the concerted elimination channel, can in general explain the observations. However, no reaction mechanism is available that can accurately predict all experimental data.

Our main objective is to develop an accurate mechanism for the $C_2H_5+O_2$ system. We started with a CBS-QB3 potential energy surface (PES) with bond additivity corrections (BAC). Tunneling corrections were included in the calculation of the high-pressure rate constants. These values are used in a chemical activation analysis to calculate pressure-dependent rate coefficients. We tested this mechanism against the wide range of experimental data and found good agreement.

Calculation Methods

The PES was calculated using the CBS-QB3 compound method as implemented in Gaussian 98W[11]. Vibrational frequencies were scaled by 0.99, and vibrational modes resembling internal rotations were replaced by a hindered rotor treatment. Standard statistical mechanics formulas were used to calculate the entropies, heat capacities and thermal contribution to the enthalpy. The electronic energies were converted to heats of formation via the atomization method. We applied bond additivity corrections, similar to the work of Petersson et al.[12] Canonical transition state theory was used to calculate high-pressure rate constants for all reaction channels with pronounced barriers. Contributions from tunneling were incorporated in high-pressure rate constants using Wigner's tunneling correction method[13]. There is no pronounced barrier found for the recombination of C_2H_5 with O_2. In this case, high-pressure rate constants were taken from Miller et al.[9]

The chemically activated reaction of $C_2H_5+O_2$ was then analyzed with the Fortran code CHEMDIS[14]. It uses QRRK theory to calculate energy dependent rate constants k(E). The collisional deactivation is described using the modified strong collision (MSC) approach. Frequency information, to calculate density of states, is provided in form of three representative frequencies with non-integer degeneracies calculated from the heat capacities. The collision parameters required for the MSC model are similar to those used by Sheng et al.[10] In addition to the MSC approach, for a few cases we used solutions of the steady state master equation as described by Sheng et al.[10] The CHEMKIN 3.6.2 package[15] is used for the numerical integration.

Results and Discussion

The major features of the PES calculated at the CBS-QB3 level of theory compare well to those reported by Sheng et al.[10] and Miller et al.[8,9] For example, we find ethylperoxy to be –34.0 kcal/mol relative to the reactants at 0K, compared to –33.9 kcal/mol given by Miller et al. The corresponding value of –34.5 kcal/mol at 298K is reasonably close to –35.3 kcal/mol reported by Sheng et al. All three studies find the barrier of the concerted elimination to be clearly below the reactants: ~2.8 kcal/mol at 0K and ~4.5 kcal/mol at 298K. The differences are somewhat larger for the isomerization reaction. Miller et al. report this barrier to be 3.2 kcal/mol above the reactants at 0K while our calculations yield 1.9 kcal/mol. Our value at 298K is within 0.2 kcal/mol of that reported by Sheng et al. On the other hand, the agreement is not so good when compared to the calculations of the Schaefer group[1].

The high-pressure rate constants calculated in this work are generally higher than those from Sheng et al.[10] The largest difference is found for the isomerization reaction where our value is ~14 times higher at 500K. Many factors may contribute to this deviation. Tunneling accounts for the increase in the rate constant by a factor of 2.7 at this temperature. Another reason may lie in differences in entropy values of the reactants and transition states. The resulting set of pressure-dependent rate coefficients together with additional reactions of peroxy radicals, chlorine and other secondary reactions, will be published elsewhere.

We compared our predictions to the pressure dependence of the overall rate constants of the $C_2H_5+O_2$ reaction observed by Kaiser et al.[3] at 298K. We found our model to underpredict the data in the falloff region by about a factor of two. Moreover, a modified mechanism using rate coefficients for the $C_2H_5+O_2$ system from Klippenstein et al.[16], which were obtained from solutions of the time dependent master equation, showed the same problem. We concluded that the energy transfer process for this system might not be correctly described by generic collision parameters, and that they might underpredict the collision efficiency of He. Thus, we increased the collision cross section by a factor of 2.4 to improve the fit to the falloff curve, and then used this value for all calculations.

Though we cannot present detailed comparisons due to space limitations, we find that our model captures the temperature and pressure dependence of the overall rate constants measured by Slagle et al.[4] Similarly, the predicted pressure dependence of the ethylene yield agrees well with measurements of Kaiser[5].

In recent experiments, Kaiser[6] measured the complex temperature dependence of the ethylene production relative to ethyl chloride. These measurements are compared to the prediction using the current model in Figure 1. We accurately predict the sharp increase in ethylene at 440K that is attributed to the thermal activation of the stabilized $CH_3CH_2OO\bullet$. Also shown are our predictions using the rate coefficients reported by Sheng et al. Their mechanism captures the overall temperature dependence but uniformly underpredicts the ethylene yield.

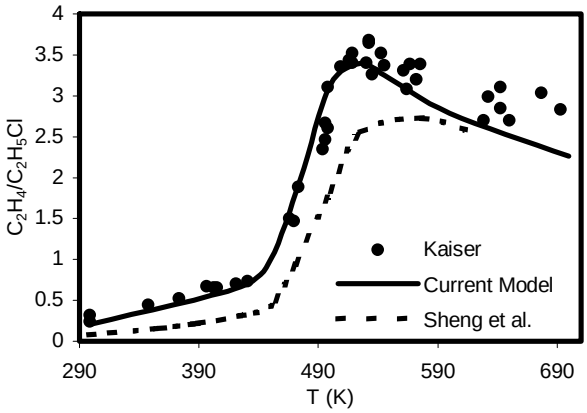

Figure 1. Comparison of the predicted temperature dependence of ethylene production to that reported by Kaiser[6] at a total density of $6.8*10^{18}$ molecules/cm^3. Values shown are the ratio of ethylene to ethyl chloride.

Ethylene oxide (C_2H_4O) is a minor product formed from $C\bullet H_2CH_2OOH$. Kaiser's[6] experimental data provide a test case to validate the relative barriers for isomerization and further reactions of the isomer. Kaiser measured the ethylene oxide production as a function of ethane conversion and of temperature. The comparison of the predicted and measured temperature dependence of the ethylene oxide yield is shown in Figure 2. Initially our model underpredicted ethylene oxide using the originally-calculated barriers. However, by decreasing the isomerization barrier by 1 kcal/mol, the predictions agree well with the measurements. This change did not affect predictions of overall rate constants as well as major products.

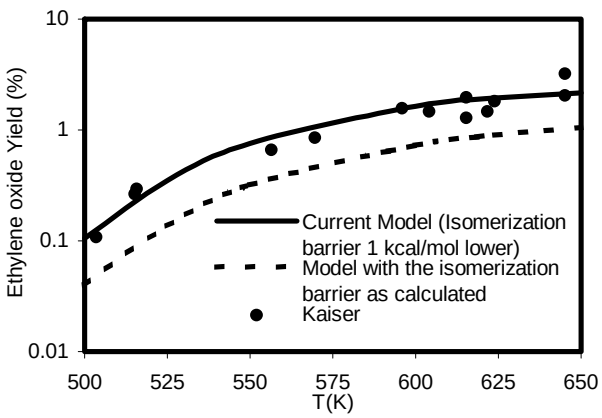

Figure 2. Comparison of the predicted temperature dependence of ethylene oxide yield to that reported by Kaiser[6] at a total density of $6.8*10^{18}$ molecules/cm^3.

Finally, we compared our model to the measurements of HO_2 production by Clifford et al.[7] Since HO_2 reacts quickly with other species, it is important to incorporate secondary reactions in the mechanism. The comparison of the predicted and measured HO_2 concentration profile relative to the initial atomic chlorine concentration at 623K is shown in Figure 3. Note that a fraction of the HO_2 is produced at very early time (due to reaction of the chemically-activated adduct). This is followed by a slower production rate (due to thermally-activated dissociation of ethylperoxy). The entire time profile is predicted accurately. Our prediction of the temperature dependence of the "total" HO_2 yield is also consistent with the measurements of Clifford et al.

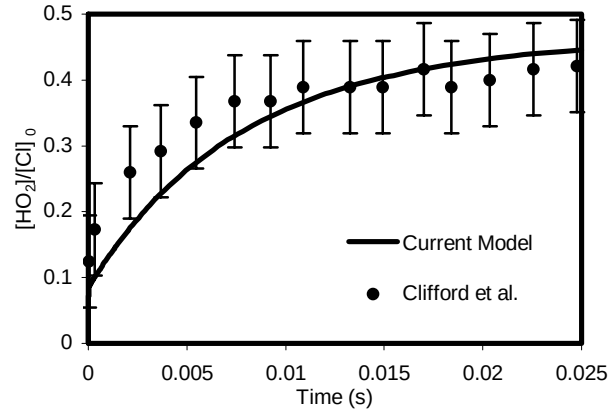

Figure 3. Comparison of the predicted HO_2 time profile relative to the initial chlorine atom concentration to that measured by Clifford et al.[7] at 623K and a total density of $9*10^{17}$ molecules/cm^3.

Conclusions

We have calculated the PES for the $C_2H_5+O_2$ system at CBS-QB3 level with BAC. Tunneling is included in high-pressure rate constants that were used in a QRRK/MSC analysis of the system. The resulting pressure-dependent reaction mechanism accurately predicts a wide range of experimental results including ethylene, HO_2 and ethylene oxide. We feel that this mechanism is suitable to be incorporated in a model of ethane oxidation at low temperatures.

References

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