COMBINATION AND DISPROPORTIONATION REACTIONS OF ALKYL RADICALS: AN AB INITIO KINETICS STUDY FOR $CH_3 + C_2H_5$

*R. S. Zhu, Z. F. Xu and M. C. Lin**

Department of Chemistry
Emory University
Atlanta, GA 30322

I. Introduction

The kinetically competitive combination and disproportionation of alkyl radicals are important to the global chemistry of hydrocarbon decomposition and combustion processes. The mechanism responsible for these reactions was a subject of much discussions[1-4] after their kinetic data had been measured extensively with the advent of the gas chromatographic technique in the 1950's.

Despite the great advance in ab intio molecular orbital and statistical rate constant calculations in recent years, reliable prediction of the product branching probabilities for the two competitive processes has not been achieved. For example, in a latest paper by Mousavipour and Homayoon[5] published in the course of our preparation for publication of this work, the critical disproportionation process has not been clearly elucidated, the corresponding barrier for this path was predicted to lie between 0.05 and 6.2 kcal/mol by different methods and its rate constant was fitted to experimental data with different energy barriers.

In this work we employed the state-of-the-art computational techniques for both electronic structure and rate constant prediction. Most significantly, the disproportionation reaction, for example, for $CH_3 + C_2H_5$ takes place via a H-bonded CH_3---H--C_2H_4 intermediate, instead of a direct transition state as reported by Mousavipour and Homayoon.[5] This mechanism is expected to be universal for the alkyl-alkyl disproportationation processes as will be demonstrated in the future for the series of the R + R' reactions (where, R = H, CH_3, …; R' = CH_3, C_2H_5,…).

II. Computational Methods

The potential energy surface (PES) was calculated at the G2M (CC2)//B3LYP/6-311+G(3df, 2p) level[6]. Some critical points are also calculated at the CCSD(T)/6-311+G(3df, 2p)//B3LYp/6-311+G(3df, 2p) level. For all the molecular orbital calculations the Gaussian 03[7] and Molpro2002.3[8] programs were used.

The rate constants were computed with microcanonical variational RRKM (Variflex)[9] and ChemRate codes.[10]

III. Results and discuss

A. Potential energy surface (PES) and mechanism

a. Abstraction reactions

$CH_4 + {}^1C_2H_4$ formation. For the direct abstract process, a relatively loose transition state was located at the B3LYP/6-311+G(3df, 2p) level. Because of the importance of the transition state barrier for the prediction of disproportionation rate constant, the barrier height of this transition state was also calculated by other methods. The results show that the barrier is around -1.6 ± 0.5 kcal/mol relative to the reactants. A loose hydrogen-bonding precursor was found to be involved in this process.

Abstraction reactions can also happen on the triplet surfaces to produce $CH_4 + {}^3C_2H_4$, $CH_4 + {}^3CH_3CH$ and ${}^3CH_2 + C_2H_6$ with higher barriers, 15.4, 15.8 and 18.4 kcal/mol, respectively.

b. Association reaction

The interaction of the two unsaturated carbon atoms in CH_3 and C_2H_5 forms association product, C_3H_8. The association energy was predicted to be 89.0 kcal/mol at the G2M (CC2) level.

c. Decomposition of chemically activated C_3H_8

H_2-elimination. The interaction of the two H atoms from the same group of CH_3 or CH_2 and from different groups in $CH_3CH_2CH_3$ will result in H_2 elimination to produce the following different products.

$H_2 + CH_3CCH_3$. The interaction of the two H atoms from the CH_2 group in C_3H_8 eliminates H_2 via a three-member-ring transition state wit a barrier above the reactants by 12.0 kcal/mol and this process has endothermicity by 5.1 kcal/mol.

$H_2 + CH_3CHCH_2$. The are two possibilities to form the products. In the first case, two H atoms, each from the CH_3 and CH_2 groups in $CH_3CH_2CH_3$, form a HHCC four-member-ring transition state with barrier above the reactants by 20.6 kcal/mol. For the second case, H_2 eliminates from one of the CH_3 groups, with simultaneously, one of the H atoms in the CH_2 group migrating to the terminal C to form $H_2 + CH_3CHCH_2$. This process has 14.8 kcal/mol barrier. The exothermicity for the reaction is 61.3 kcal/mol.

H_2 + cyc-C_3H_6. In this channel, the two C-H bonds in CH_3 groups of $CH_3CH_2CH_3$ intermediate are lengthening to form a H-H bond, meanwhile, the two C atoms from the CH_3 groups are connecting to form a C-C bond. Although this is an exothermic process with exothermicity of 52.7 kcal/mol, it has a much higher barrier, 58.9 kcal/mol above the reactants, it will not be kinetically important.

CH_2 elimination. In this channel, one of the H atoms in the CH_3 group of $CH_3CH_2CH_3$ can migrate to the CH_2 group via a three-member-ring transition state to form a loose complex with a barrier of 14.5 kcal/mol above the reactants. The complex lies above the reactants by 11.7 kcal/mol, which further dissociates to produce ${}^1CH_2 + C_2H_6$ with endothermicity of 15.1 kcal/mol.

CH_4-elimination. There are two possible ways to eliminate CH_4 from $CH_3CH_2CH_3$.

$CH_4 + CH_2CH_2$. In this channel, one H atom migrates from one CH_3 groups to the other CH_3 group, simultaneously, one of the C-C bond is breaking via a four-member-ring transition state to form the products with a barrier lying above the reactants by 23.7 kcal/mol. Apparently, this channel is not competitive with the direct abstraction one as discussed in the previous section.

CH_4 + CH_3CH. This path involves one H atom in the CH_2 group transferring to one of the CH_3 group via a three-center transition state to form a loose complex which dissociates to produce products $CH_4 + CH_3CH$. The transition state, complex and products lie above the reactants by 5.7, 2.4 and 2.8 kcal/mol, respectively.

B. Rate constant calculations

The rate constants for those channels with barriers less than 15.0 kcal have been calculated. The results show that the dominant channel in the temperature range of 200 – 3000 K is C_3H_8 formation. The predicated rate constants for association, dissociation processes and the ratio of combination/disproportionation are in reasonable agreement with available values.

IV. Conclusions

Complete potential energy surface (PES) for the reaction of $CH_3 + C_2H_5$ has been calculated at the G2M (CC2)//B3LYP/6-311+G(3df, 2p) level. Rate constant calculations show that formation of C_3H_8 is dominant in the temperature range of 200 ~ 3000 K. Predicted rates reasonably agree with experimental data.

Acknowledgement

This work is sponsored by DOE. Acknowledgment is also made to the Cherry L. Emerson Center of Emory University for the use of its resources, which are in part supported by a National Science Foundation grant (CHE-0079627) and an IBM Shared University Research Award.

References

(1) Konar, R. S. *Int. J. Chem. Kinet.* **1970**, *2 (5)*, 419.
(2) Laidler, K. J. *Int. J. Chem. Kinet.* **1971**, *3*, 377.
(3) Konar, R. S. *Int. J. Chem. Kinet.* **1971**, *3*, 379.
(4) Dannenberg, J. J. and Baer, B., *J. Am. Chem. Soc.* **1987**, *109*, 292.
(5) Mousavipour, S. H.; Homayoon, Z. *J. Phys. Chem. A* **2003**, *107*, 8566.
(6) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*,7414.
(7) M. J. Frisch, M. J. et al., *GAUSSIAN 03, REVISION B.0*1; Gaussian, Inc., Pittsburgh PA, **2003**.
(8) MOLPRO is a package of *ab initio* programs written by H.-J. Werner et al.
(9) Klippenstein, S. J. ; Wagner, A. F.; Dunbar, R. C. ; Wardlaw, D. M. and Robertson, S. H. VARIFLEX: VERSION **1.00**, **1999**.
(10) Mokrushin, V.; Bedanov, V.; Tsang, W.; Zachariah, M. R.; Knyazev, V. D. *ChemRate, Version 1.19*; National Institute of Standards and Technology: Gaithersburg, MD 20899, **2002.**