Ab Initio quantum chemical studies of hydrogen abstraction reactions of hydrocarbons

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Introduction

The accurate prediction of kinetic parameters of hydrogen abstraction reactions of hydrocarbons is of fundamental importance to the kinetic modeling of the commercial processing of natural gas, petroleum, and its derivatives[1], as well as their combustion reactions.[2,3] Results of *ab initio* calculations will be reported here for the reactions $C_2H_6 + H\bullet \rightarrow C_2H_5\bullet + H_2$ and $C_2H_6 + CH_3\bullet \rightarrow C_2H_5\bullet + CH_4$. Reactions of propane will be also discussed in the talk.

Methods

Structures and vibrational frequencies were calculated at the HF/DZP level of theory. Activation energies were obtained at various levels of theory, the highest being MP4/pVTZ//HF/DZP. Morokuma's ONIOM method[4] was also used to find activation energies, using a two layer strategy. The abstracting species, the carbon from which the hydrogen atom was being abstracted, and the other hydrogens attached to that carbon were in the high level layer; all other atoms were in the low level layer. Calculations were done using Gaussian 98[5] running on PC workstations.

Results and Discussion

Previous calculations have shown that accurate activation energies can be obtained for reactions of this type from structures calculated at the HF/DZP level, as long as correlated calculations are done, preferably with a large basis set, for the energetics.[6] Figure 1 gives the calculated HF/DZP structures. Subsequent vibrational frequency calculations yielded only one imaginary frequency for each reaction, the normal modes of which were along the reaction coordinate.

Table 1 gives activation energies at various levels of theory and compares these to experiment. The ONIOM results are seen to give activation energies within 1-2 kcal/mol. For comparison the MP4/pVTZ//HF/DZP activation energy for the reaction of $C_2H_6 + H\bullet$ (without using ONIOM) was found to be 11.2 kcal/mol, less than one kcal/mol closer to the experimental value. This latter calculation took nearly 7 hours on a Pentium II PC and used 900 mbytes of scratch disk, whereas the ONIOM calculation only took 19 minutes and 200 Mbytes.

Table 1. Activation Energies (kcal/mol)

Level of Theory	$C_2H_6 + H\bullet$	$C_2H_6 + CH_3\bullet$
HF/DZP	20.0	29.6
MP2/DZP//HF/DZP	15.1	16.7
MP4/DZP//HF/DZP	13.8	17.2
ONIOM*	11.8	16.4
Experiment[7]	10.8	14-15

*MP4/pVTZ for the high level; HF/DZP for the low level

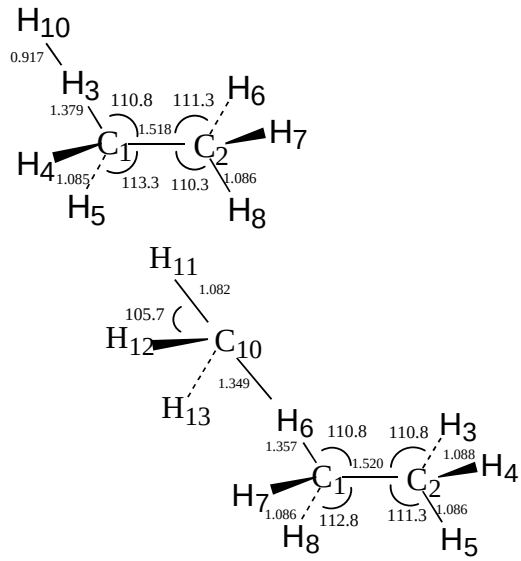

Figure 1. HF/DZP transition state structures for $C_2H_6 + H\bullet \rightarrow C_2H_5\bullet + H_2$ and $C_2H_6 + CH_3\bullet \rightarrow C_2H_5\bullet + CH_4$. Bond lengths are in Å and bond angles are in degrees.

Transition State Theory Calculations

Reaction rate coefficients were calculated using transition state theory (TST) and results from the *ab initio* calculations shown in Table 1. Corrections for barrier tunneling were determined using parabola and the Eckart potential approximations. These calculations were performed using the TS Rate program. The evaluated rate several approximations, including Wigner's, Bell's truncated coefficients for the two hydrogen abstraction reactions are presented in Figures 2 and 3, respectively. The calculated rate coefficient increases with the application of the barrier tunneling corrections. The Wigner approximation, which is applicable for small tunneling corrections near the top of the barrier and does not depend directly on the barrier height, yields the smallest correction and is considered to be inadequate where significant tunneling occurs. Similarly, the truncated parabola, which approximates the barrier as a symmetric parabola, also may only adequately describes the barrier near its top. This correction method is also only applicable for small tunneling corrections. It also appears to grossly over-estimate the tunneling correction where significant tunneling is likely to occur, i.e. at lower temperatures. The Eckart potential function provides a better description of the barrier and the tunneling correction factors are intermediate between the Wigner and Bell approximation corrections.

The calculated results were fitted to the three parameter modified Arrhenius equation to obtain a better fit of the results. The rate coefficient expression has the form

$$\log(k, \mathrm{M^{-1}s^{-1}}) = A - \frac{B}{T} + C\log(T) \qquad (1)$$

where T is the temperature in K. The parameters for the rate expressions for the reactions $C_2H_6 + H\bullet$ and $C_2H_6 + CH_3\bullet$ are given below in Tables 2 and 3, respectively.

These rate coefficient results, except for results obtained using the Bell correction method, were compared to available data from the literature. This comparison is shown in Figures 4 and 5 for the reactions $C_2H_6 + H\bullet$ and $C_2H_6 + CH_3\bullet$, respectively. The calculated results are in better agreement with literature data for the reaction $H\bullet + C_2H_6$ than for $CH_3\bullet + C_2H_6$.

Table 2. Rate Expression Parameters for C_2H_6 + H•

Correction Method	A	B	C
Uncorrected	5.161	2341	1.96
Wigner	5.250	2090	1.90
Bell	-13.920	-556	7.37
Eckart Potential	-7.269	413	5.49

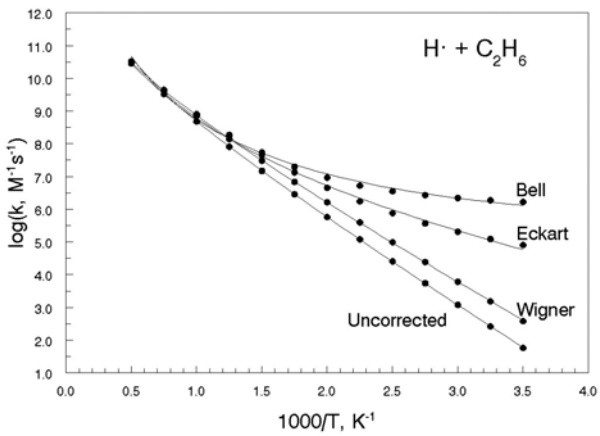

Figure 2. Plot of calculated transition state theory rate coefficients versus temperature for H• + C_2H_6. Corrections for barrier tunneling employing the Wigner, Bell and Eckart approximation methods applied to the uncorrected results.

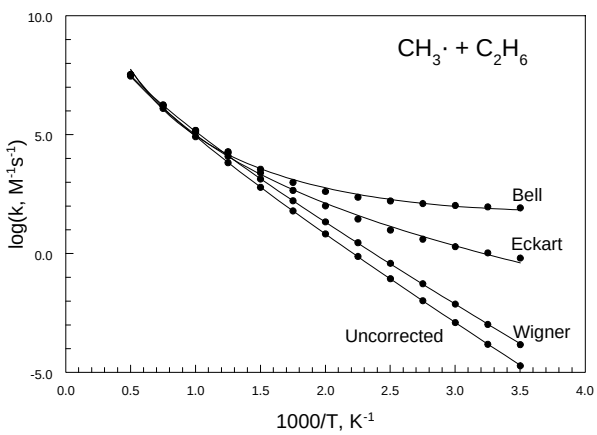

Figure 3. Plot of calculated transition state theory rate coefficients versus temperature for CH_3• + C_2H_6. Corrections for barrier tunneling employing the Wigner, Bell and Eckart approximation methods applied to the uncorrected results.

Table 3. Rate Expression Parameters for C_2H_6 + CH_3•

Correction Method	A	B	C
Uncorrected	-1.173	3178	3.09
Wigner	-0.819	2927	2.96
Bell	-30.205	-1217	11.31
Eckart Potential	-20.703	270	8.66

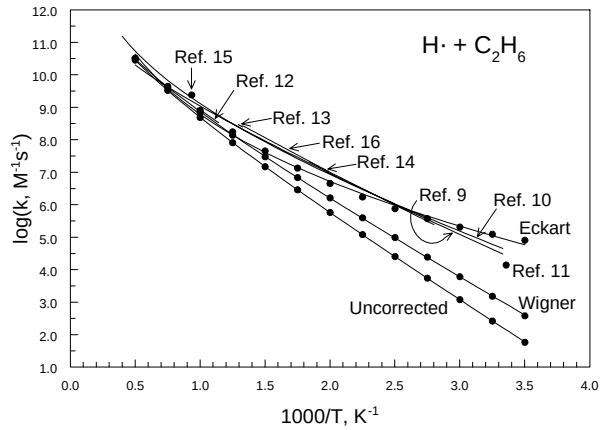

Figure 4. Comparison of calculated transition state theory rate coefficients versus temperature for H• + C_2H_6 and literature data.

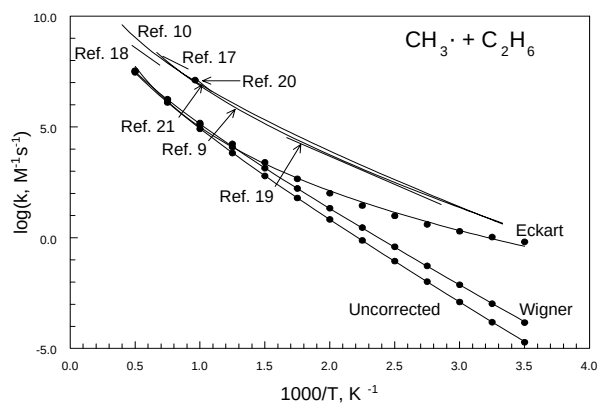

Figure 5. Comparison of calculated transition state theory rate coefficients versus temperature for CH_3• + C_2H_6 and literature data.

References

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