J. Phys. Chem. A **2009,** *113,* 11679–11684

Accurate Coupled Cluster Calculations of the Reaction Barrier Heights of Two $CH_3^{\bullet} + CH_4$ Reactions[†]

Wim Klopper,*[,§] Rafał A. Bachorz,[§] David P. Tew,[§] Jorge Aguilera-Iparraguirre,[§] Yannick Carissan,[⊥] and Christof Hättig[‡]

Institut für Physikalische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany, Universités d'Aix-Marseille I, II & III—CNRS, UMR 6263: Institut des Sciences Moléculaires de Marseille (iSm2), F-13397 Marseille Cedex 20, France, and Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Received: March 26, 2009; Revised Manuscript Received: July 3, 2009

We have computed barrier heights of 71.8 ± 2.0 and 216.4 ± 2.0 kJ mol^{-1} for the reactions $CH_4 + CH_3^{\bullet} \rightarrow CH_3^{\bullet} + CH_4$ and $CH_4 + CH_3^{\bullet} \rightarrow H^{\bullet} + C_2H_6$, respectively, using explicitly correlated coupled cluster theory with singles and doubles combined with standard coupled cluster theory with up to connected quadruple excitations. Transition-state theory has been used to compute the respective reaction rate constants in the temperature interval of 250−1500 K. The computed rates for the reaction to ethane are orders of magnitude slower than those used in the mechanism of Norinaga and Deutschmann (*Ind. Eng. Chem. Res.* **2007**, *46*, 3547.) for the modeling of the chemical vapor deposition of pyrolytic carbon.

1. Introduction

Recently, Norinaga and Deutschmann modeled the chemical kinetics of the pyrolysis of the hydrocarbons ethylene, acetylene, and propylene under conditions relevant to the chemical vapor deposition (CVD) of pyrolytic carbon.[1] For this modeling, they had developed a mechanism containing 227 species and 827 reactions. One of these was

$$CH_4 + CH_3^{\bullet} \rightarrow C_2H_6 + H^{\bullet}$$

which contributed to the mechanism with the reaction rate constant

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

with $A = 8.0 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, $n = 0$, and $E_a = 167.37$ kJ mol^{-1}. The parameters were taken from the work of Tabayashi and Bauer.[2] Note that these parameters are fit parameters that were adjusted by requiring the best overall agreement between observed density gradient profiles and those obtained from calculations based on a 12 step decomposition mechanism for the pyrolysis of methane.[2] The above reaction was considered by Kassel[3] almost 75 years ago when discussing the role of methyl and methylene radicals in the decomposition of methane. The reaction was also discussed in 1959 by Skinner and Ruehrwein,[4] who crudely estimated the rate constant as $k = 10^9 T \exp\{-E_a/(RT)\}$ cm^3 mol^{-1} s^{-1}, with $E_a = 188.28$ kJ mol^{-1} (average of 40−50 kcal mol^{-1}). On the basis of this estimate, these authors concluded that the reaction can be neglected in a mechanism for the pyrolysis of methane.[4] Furthermore, more than 25 years ago, Back[5] derived an upper limit for the reaction rate constant of $k = 63$ cm^3 mol^{-1} s^{-1} at 802 K, about 16 times below the value of Tabayashi and Bauer for that same temperature. Hence, the role of this reaction in the mechanism of Norinaga and Deutschmann was considered to be suspicious, and we decided to reinvestigate it by means of modern, high-level ab initio quantum chemical methods.

In the present work, we show that the production of ethane from the reaction of methane with methyl is grossly overestimated by the above rate constant. From transition-state theory (TST) and highly correlated ab initio calculations, we find rates that are between 3 (at 1500 K) and 10 (at 300 K) orders of magnitudes slower than those used by Norinaga and Deutschmann.[1] This leads us to conclude that the role of this reaction in the mechanism must be reexamined. Furthermore, we show that the barrier height for the above reaction to C_2H_6 and $H^{\bullet}$ is much higher (about 3 times higher) than the barrier height for another reaction between the two reactants, the reaction in which a hydrogen is abstracted from methane by a methyl radical.

A second purpose of the present work is to assess the performance of the explicitly correlated coupled cluster model CCSD(F12) that we have recently implemented in the Turbomole program package.[6,7] This model has the potential to yield electronic molecular energies at the level of coupled cluster theory with single and double excitations (CCSD)[8,9] at the limit of a complete one-particle basis set. In conjunction with corrections for higher excitations (connected triples and connected quadruples), it should be possible to compute the barrier height for the above reaction with an accuracy of about 1−2 kJ mol^{-1}, that is, with an error of about 0.5−1.0%.

The CCSD(F12) model was first introduced as the CCSD(R12) approximation[10] to the full CCSD-R12 approach.[11] Here, we indicate by writing "R12" that in this initial work, explicitly correlated two-particle basis functions of the form

---

[†] Part of the "Walter Thiel Festschrift".

* To whom correspondence should be addressed. E-mail: klopper@chem-bio.uni-karlsruhe.de.

[§] Universität Karlsruhe (TH).

[⊥] Universités d'Aix-Marseille I, II & III—CNRS.

[‡] Ruhr-Universität Bochum.

10.1021/jp902753s CCC: \$40.75

$$\chi_{ij}(1,2) = r_{12}\varphi_i(1)\varphi_j(2) \qquad (2)$$

were used, where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the electrons 1 and 2 and where φ_i and φ_j are two spin orbitals that are occupied in the Hartree−Fock reference determinant. More recently, the R12-type two-particle basis functions were replaced by functions of the type

$$\chi_{ij}(1,2) = f(r_{12})\varphi_i(1)\varphi_j(2) = \exp(-\gamma r_{12})\varphi_i(1)\varphi_j(2) \qquad (3)$$

also called Slater-type geminals (STG).[12] We will refer to the corresponding approach as the CCSD(F12) model.[13]

The CCSD(F12) model as well as the full CCSD-F12 approach and other simplifications of it are currently being implemented in various quantum chemistry programs,[14−25] also in combination with connected triples and higher excitations. In particular, Köhn and co-workers[17] have shown that the CCSD(F12) model is an excellent approximation to the full CCSD-F12 approach, and the CCSD(F12) model is the method of choice that we have implemented in the Turbomole program. The present work reports on one of the first applications of CCSD(F12) theory with chemical relevance. In such a real-life application, CCSD(F12) calculations are combined with a series of other coupled cluster calculations including geometry optimizations, calculations of harmonic vibrational frequencies, and coupled cluster calculations with connected triples and quadruples. Within the whole set of calculations that must be performed, the CCSD(F12) calculations take only a fraction of the total computation time, and therefore, in an application as the one presented here, there appears to be no need to further simplify the CCSD(F12) model.

The present work is organized as follows. In section 2, we present the details of the ab initio calculations of the reaction barriers (section 2.1) and of the reaction rate constants by means of transition-state theory (section 2.2). Accordingly, the results are presented in section 3, both for the reaction barriers (section 3.1) and the reaction rate constants (section 3.2). Conclusions are collected in section 4.

2. Computational Details

2.1. Reaction Barriers. The geometries of $CH_3^\bullet$, CH_4, C_2H_6, $[H\cdots C_2H_6^\bullet]^\ddagger$, and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$ were optimized at the all-electron (ae) CCSD(T)/aug-cc-pwCVTZ level[26−28] using the ACES II program package.[29] For the open-shell systems, an unrestricted Hartree−Fock (UHF) reference determinant was used. The optimized equilibrium C−H distances in $CH_3^\bullet$, CH_4, and C_2H_6 are 107.78, 108.80, and 109.08 pm, respectively. In ethane, the optimized C−C bond amounts to 152.60 pm and the C−C−H angle to 111.20°. The equilibrium structures of the two transition states are depicted in Figure 1. Our equilibrium structures of $[H\cdots C_2H_6^\bullet]^\ddagger$ and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$ compare well with those obtained by Layfield et al.[30] and Remmert and co-workers,[31] respectively.

Single-point energy calculations were performed at the ae-CCSD(T)/aug-cc-pwCVQZ′ level, where the prime indicates that the aug-cc-pwCVQZ basis was used for C but only the aug-cc-pVTZ basis for H. For comparison, frozen core (fc) calculations were performed to quantify core−valence (CV) correlation effects. The 1s orbitals of C were kept frozen in the fc calculations.

Further single-point energy calculations were performed at the fc-CCSDT/aug-cc-pVDZ and fc-CCSDT(Q)/cc-pVDZ levels[32−36] using the MRCC program package.[37,38]

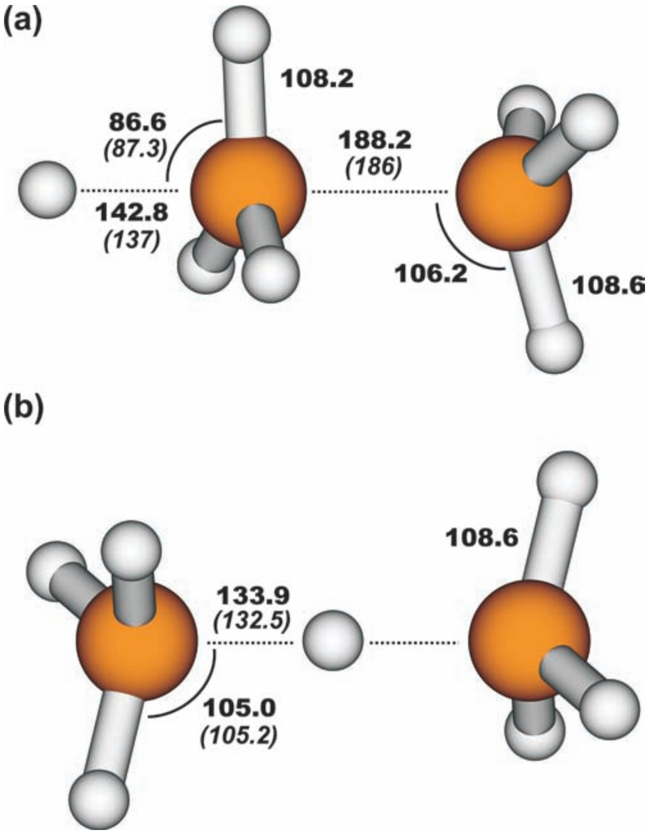

Figure 1. Equilibrium structures of the transition structures (a) $[H\cdots C_2H_6^\bullet]^\ddagger$ (C_{3v} symmetry) and (b) $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$ (D_{3d} symmetry) as obtained at the ae-CCSD(T)/aug-cc-pwCVTZ level. Geometry parameters from the work of Layfield et al.[30] and Remmert et al.[31] are shown in parentheses. Bond lengths are given in pm and angles in degrees.

Explicitly correlated coupled cluster calculations were performed at the fc-CCSD(F12)/cc-pVQZ-F12 level using the Turbomole program package.[7] The exponent of the Slater-type geminal was $\gamma = 1.1\ a_0^{-1}$, which is the optimal exponent for the cc-pVQZ-F12 basis set.[39] We employed the complementary auxiliary basis set approach (CABS) of Valeev[40] using the auxiliary basis set of Yousaf and Peterson[41] optimized for the cc-pVQZ-F12 atomic orbital basis set. For the two-electron integrals, computed employing the density-fitting technique,[42] we used the aug-cc-pwCV5Z MP2 fitting basis of Hättig.[43] To represent the Fock operator within the CCSD(F12) calculations, we used the aug-cc-pV5Z JK fitting basis of Weigend.[44] The orbital-invariant version of CCSD(F12) theory was used.[13]

The cc-pVDZ, aug-cc-pVXZ (X = D, T, Q), and aug-cc-pwCVXZ (X = T, Q) basis sets[45−47] were obtained from the Basis Set Library of the Environmental Molecular Sciences Laboratory.[48,49] The cc-pVQZ-F12 sets with corresponding CABS were downloaded from the Website of Peterson.[50]

Corrections for scalar-relativistic effects (one-electron Darwin and mass−velocity terms, MVD) were calculated at the ae-CCSD(T)/aug-cc-pwCVTZ level.[51,52] For the C atom, the spin−orbit correction (SO) to the total electronic energy amounts to $\Delta E_{SO} = -0.35399$ kJ mol^{-1}.[53]

2.2. Reaction Rates. Simple transition-state theory is used for the calculation of the reaction rate constants. The well-known expression for the reaction rate constant of a bimolecular reaction $X + Y \rightleftarrows XY^\ddagger$ is[54]

$$k = \kappa \frac{k_bT}{h} \frac{(q^{\ddagger}_{XY}/V)}{(q_X/V)(q_Y/V)} \exp\left(\frac{-\Delta E_{B,0}}{RT}\right) \qquad (4)$$

where $q^{\ddagger}_{XY}$, q_X, and q_Y are the dimensionless partition functions (including translational, vibrational, and rotational contributions) of the transition state and the reactants, respectively (using the harmonic oscillator and rigid rotor approximation and correcting for internal hindered rotations). The degeneracies of the doublet states are not considered since they cancel out in eq 4. R is the gas constant, k_b the Boltzmann constant, h the Planck constant, and V the volume that cancels the volume in the translational partition function

$$q_{trans} = \left(\frac{2\pi m k_b T}{h^2}\right)^{3/2} V \qquad (5)$$

where m is the mass of the molecule or radical. $\Delta E_{B,0}$ is the electronic barrier height $\Delta E_{B,e}$ plus the zero-point vibrational energy (ZPVE). The ZPVE is computed at the ae-CCSD(T)/aug-cc-pwCVTZ level. κ is the transmission coefficient accounting for tunneling effects, computed from the Wigner formula[55]

$$\kappa = 1 - \frac{1}{24}\left(\frac{h\nu}{k_bT}\right)^2\left(1 + \frac{RT}{\Delta E_{B,0}}\right) \qquad (6)$$

Only the imaginary frequency ν associated with the reaction coordinate and the reaction barrier $\Delta E_{B,0}$ are required to calculate κ. At the ae-CCSD(T)/aug-cc-pwCVTZ level, the imaginary frequencies are 1540.4i and 1855.9i cm^{-1} for $[H\cdots C_2H_6^\bullet]^\ddagger$ and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$, respectively.

Corrections accounting for hindered rotations are included for rotations about the C−C bond and about the reaction coordinate C···H···C. To obtain these corrections, we computed the potential energy of the hindered internal rotor,

$$V(\phi) = \frac{V_s}{2}[1 - \cos(3\phi)] \qquad 0 \le \phi \le 2\pi \qquad (7)$$

at the level of ae-CCSD(T)/aug-cc-pwCVTZ theory, optimizing all geometry parameters except ϕ. At this level, the barrier heights V_s are 11.74, 6.56, and 0.22 kJ mol^{-1} for C_2H_6, $[H\cdots C_2H_6^\bullet]^\ddagger$, and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$, respectively. Each reduced moment of inertia was computed from the distances (in the equilibrium geometry) of the rotating H atoms from the axis of rotation. These distances amount to 101.70, 104.28/108.01, and 104.84 pm for C_2H_6, $[H\cdots C_2H_6^\bullet]^\ddagger$, and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$, respectively (Table 1). The eigenvalues of the Schrödinger equation with the potential eq 7 were obtained by diagonalizing a tridigonal matrix of dimension 501, following recent work by Strekalov.[56] In eq 4, the vibrational partition functions are computed with respect to the corresponding lowest vibrational level ($v = 0$) as the zero of energy. This yields

$$q_{vib} = \prod_{k=0}^{n} [1 - \exp(-\Theta_k/T)]^{-1} \qquad (8)$$

where the product runs over all real harmonic frequencies with characteristic vibrational temperatures Θ_k. This vibrational partition function is corrected for hindered internal rotation by multiplying by the factor

$$q_{hr}/q_{tors} = q_{hr}[1 - \exp(-\Theta_{tors}/T)] \qquad (9)$$

where q_{hr} is the partition function of the hindered internal rotor and q_{tors} the partition function of the harmonic torsional vibration, both evaluated with respect to their own lowest level as the zero of energy. The difference between the zero-point energies of the one-dimensional harmonic oscillator and the hindered internal rotor is taken into account when calculating the electronic energy (column HR in Table 2).

TABLE 1: Rotational Barriers (V_s) and Constants (B)

system	V_s/kJ mol^{-1}	R_{XH}[a]/pm	B/kJ mol^{-1}	Θ_{tors}[b]/K
C_2H_6	11.74	101.70	0.129	447.7
$[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$	0.22	104.84	0.121	61.2
$[H\cdots C_2H_6^\bullet]^\ddagger$	6.56	104.28 108.01	0.118	321.0

[a] Distance of the H atom from the axis of rotation. [b] Characteristic vibrational temperature of the torsional vibration.

3. Results

3.1. Reaction Barriers. For the five species involved in this study, the computed electronic atomization energies (AE, the dissociation energy $\sum D_0$ for the dissociation into isolated atoms) are given in Table 2 and compared with literature values[57,58] where possible. The latter originate from the Active Thermochemical Tables (ATcT) of Ruscic.[59−62]

The computed AEs are found to be 1.3, 2.6, and 2.9 kJ mol^{-1} below the ATcT reference values for $CH_3^\bullet$, CH_4, and C_2H_6, respectively. One reason for these discrepancies is that in the present work, we have only included (except for the hindered rotor treatment) the harmonic ZPVE. For example, the anharmonic correction to the ZPVE of $CH_3^\bullet$ amounts to 0.9 kJ mol^{-1} at the ae-CCSD(T)/cc-pCVTZ′ level.[57] Taking this anharmonic correction into account would have produced a theoretical AE for $CH_3^\bullet$ of 1209.3 kJ mol^{-1}, within 0.4 kJ mol^{-1} of the experimental value. The total ZPVE contribution would have been −77.4 kJ mol^{-1}, in good agreement with the value (−77.6 kJ mol^{-1}) of Schwenke.[63] For methane, Schwenke's value[64] amounts to −116.1 kJ mol^{-1}, whereas our harmonic value is −117.9 kJ mol^{-1}. Taking Schwenke's value in place of ours would reduce the error in the calculated AE of methane from 2.6 to 0.8 kJ mol^{-1}. For ethane, an accurate (anharmonic) ZPVE contribution of −194.1 kJ mol^{-1} is available from benchmark calculations performed by Karton and co-workers.[65] This contribution is 2.6 kJ mol^{-1} smaller in magnitude than our harmonic value, which makes up for almost all of the error of 2.9 kJ mol^{-1}. Furthermore, our fc-CCSD(T) value of 2972.5 kJ mol^{-1} compares well with the value of 2973.7 kJ mol^{-1} obtained at the W4 level[66] by these authors.

We expect that the errors due to neglecting the anharmonic corrections to the ZPVE will largely cancel when we compute the relative quantities of interest such as reaction energies and barrier heights. The calculated energy of reaction for the endothermic reaction

$$CH_4 + CH_3^\bullet \rightarrow C_2H_6 + H^\bullet$$

for instance, amounts to 63.7 kJ mol^{-1}, only 1.0 kJ mol^{-1} below the ATcT value of 64.7 kJ mol^{-1}. The anharmonic corrections

TABLE 2: Electronic Atomization Energies[a] (kJ mol^{-1})

system	CCSD	(T)	(Q)	CV	ZPVE	HR	MVD	SO	total	ATcT
$CH_3^\bullet$	1275.1	7.6	0.5	4.5	−78.3		−0.7	−0.4	1208.4	1209.7[b]
CH_4	1741.0	11.9	0.5	5.3	−117.9		−0.8	−0.4	1639.6	1642.2[c]
C_2H_6	2945.8	26.2	0.9	10.3	−196.7	0.1	−1.7	−0.7	2784.3	2787.2[c]
$[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$	2933.2	27.7	1.9	9.5	−194.0	0.2	−1.6	−0.7	2776.2	
$[H\cdots C_2H_6^\bullet]^\ddagger$	2787.2	33.4	2.6	8.9	−198.4	0.1	−1.6	−0.7	2631.6	

[a] The CCSD energies were obtained at the fc-CCSD(F12)/cc-pVQZ-F12 level. The corrections for connected triple excitations (T) were obtained at the fc-CCSD(T)/aug-cc-pwCVQZ′ level. The correction (Q) for connected quadruples contains the difference CCSDT − CCSD(T) calculated at the fc-CCSDT/aug-cc-pVDZ level and the (Q) term obtained at the fc-CCSDT(Q)/cc-pVDZ level. The correction for core−valence correlation (CV) was obtained at the ae-CCSD(T)/aug-cc-pwCVQZ′ level. The harmonic zero-point vibrational energy (ZPVE) correction is supplemented by a zero-point energy correction for hindered rotation (HR), and both scalar relativistic (MVD) and spin−orbit (SO) effects are taken into account. [b] Taken from the work of Aguilera-Iparraguirre and co-workers.[57] [c] Taken from the work of Klopper and co-workers.[58]

TABLE 3: Logarithm of the Reaction Rate Constant, log(k/[cm^3 mol^{-1} s^{-1}]), as a Function of Temperature for the Reactions $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ (reaction 1) and $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$ (reaction 2) along with the Transmission Coefficient κ Accounting for Tunneling Effects

	reaction **1**		reaction **2**		
T/K	this work	κ	this work	κ	used in ref 1
300	0.20	4.42	−25.38	3.30	−15.24
400	3.13	2.94	−16.18	2.30	−7.95
500	4.92	2.26	−10.63	1.83	−3.58
600	6.14	1.88	−6.89	1.58	−0.67
700	7.05	1.66	−4.20	1.43	1.41
800	7.75	1.51	−2.15	1.33	2.98
900	8.31	1.41	−0.54	1.26	4.19
1000	8.78	1.33	0.76	1.21	5.16
1100	9.17	1.28	1.84	1.18	5.96
1200	9.51	1.23	2.75	1.15	6.62
1300	9.81	1.20	3.53	1.13	7.18
1400	10.07	1.18	4.21	1.11	7.66
1500	10.30	1.15	4.80	1.10	8.07

to the transition states with their partially broken bonds may be somewhat larger than those for the molecules $CH_3^\bullet$, CH_4, and C_2H_6, but they are difficult to quantify. The lowest-energy vibrational modes not accounted for in the hindered rotor treatments have wavenumbers of 317 ($[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$) and 640 cm^{-1} ($[H\cdots C_2H_6^\bullet]^\ddagger$). Scaling all of the harmonic vibrational frequencies by a factor of 0.987, which yields an anharmonic correction to the AEs of $CH_3^\bullet$, CH_4, and C_2H_6 of the correct order of magnitude, would affect the reaction barrier heights only by ~0.03 kJ mol^{-1} and the log(k) values in Table 3 only by about 0.02.

Similar error cancellations occur for other (small) ignored effects and remaining errors. For example, the diagonal Born−Oppenheimer correction (DBOC) can crudely be estimated to contribute ~0.1 kJ mol^{-1} per CH bond to the AEs of the systems studied here[58] and can thus safely be neglected when computing reaction energies and barrier heights. Another example is the basis set error in the (T) corrections, which can be estimated from an extrapolation from aug-cc-pwCVQZ′ and aug-cc-pwCVTZ results using the X^{-3} formula of Helgaker and co-workers.[67] This increases the (T) contributions to the AEs by 0.2 kJ mol^{-1} for $CH_3^\bullet$ and CH_4 and by 0.5 kJ mol^{-1} for C_2H_6, $[H\cdots C_2H_6^\bullet]^\ddagger$, and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$. (Note that the (T) contribution for ethane computed by Karton et al.[65] is also ~0.5 kJ mol^{-1} larger than ours.) Thus, the effect of the (T) basis set error on the relevant relative quantities is only on the order of 0.1 kJ mol^{-1} and thus negligible. The cancellation of small terms is even more striking for the Hartree−Fock corrections that are contained in our CCSD(F12) values. These corrections are computed as second-order perturbation theory corrections from single excitations into the complementary auxiliary basis set (CABS) that is used in the CCSD(F12) model.[14] The corresponding contributions to the AEs amount to 0.14, 0.18, 0.29, 0.31, and 0.31 kJ mol^{-1} for $CH_3^\bullet$, CH_4, C_2H_6, $[H\cdots C_2H_6^\bullet]^\ddagger$, and $[CH_3\cdots H\cdots CH_3^\bullet]^\ddagger$, respectively, with virtually no net effect on the reaction energies and barrier heights. These Hartree−Fock corrections could just as well have been omitted.

Also the other terms are either so accurate or so small that we can rely on a cancellation of the remaining errors in these terms. Concerning the CV correction, our values for $CH_3^\bullet$, CH_4, and C_2H_6 (4.5, 5.3, and 10.3 kJ mol^{-1}) agree well with the corresponding values from W4 theory (4.56, 5.31, and 10.2 kJ mol^{-1}).[65,66] The sum of our CCSD, (T), and CV terms gives an atomization energy of 1287.4 kJ mol^{-1} for $CH_3^\bullet$ (after adding 0.2 kJ mol^{-1} from extrapolating the (T) correction). This compares favorably with the value of 1288.0 kJ mol^{-1} obtained at the HEAT-456 level by Harding et al.,[68] which contains inner-shell correlation. Our MVD contributions agree to within 0.05 kJ mol^{-1} with those of the W4 and HEAT protocols.[65,66,68] Correlation effects beyond the CCSD(T) level, however, seem somewhat larger (e.g., by about a factor of 2 for ethane)[65] in our calculations than those in the W4 and HEAT-456(Q) protocols, but the corresponding contributions to the reaction energies and barrier heights are very small.

In view of all of the above considerations, we expect that our computed reaction barrier heights are accurate to within 2 kJ mol^{-1}. Our final values are thus $\Delta E_{B,0} = 71.8 \pm 2.0$ and 216.4 ± 2.0 kJ mol^{-1} for the reactions $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ and $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$, respectively. Concerning the latter reaction, we obtain $\Delta E_{B,0} = 152.7 \pm 2.0$ kJ mol^{-1} for the backward reaction, remarkably close to but slightly smaller than the CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVDZ value of 155.0 kJ mol^{-1} computed (presumably in the frozen core approximation) by Layfield and co-workers.[30] Also, our computed barrier height for the reaction $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ (71.8 ± 2.0 kJ mol^{-1}) is slightly below those obtained by Remmert et al.[31] (74.1 kJ mol^{-1} at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level) and Kungwan and Truong[69] (75.7 kJ mol^{-1} at the CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVDZ level).

3.2. Reaction Rates. Computed reaction rate constants (or rather the logarithm thereof) are shown in Table 4 for the reactions $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ (reaction **1**) and $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$ (reaction **2**). They are also depicted in Figure 2, which not only shows the calculated rate constants at 300, 350,..., 1500 K but also the curves that are obtained by fitting expressions of the type of eq 1 to the calculated points in the range of 600−1500 K. In Figure 2, the solid line corresponds to the reaction rate constants used in ref 1, that is, using eq 1 with the parameters of Tabayashi and Bauer.[2] Our rate constants

TABLE 4: Fitting Parameters Obtained by Adjusting the Rate Constant Equation $k = AT^n \exp\{-E_a/(RT)\}$ to the Calculated Values in the Range of 600−1500 K

reaction	A/cm^3 mol^{-1} s^{-1}	n	E_a/kJ mol^{-1}
$CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$	1.5×10^2	3.2	55
$CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$	4.3×10^1	3.2	200
$H^\bullet + C_2H_6 \rightarrow CH_4 + CH_3^\bullet$	1.2×10^8	1.7	145

are below the upper limit of Back[5] at 802 K and below the rate constant expression of Skinner and Ruehrwein.[4]

The parameters A, n, and E_a, obtained by fitting computed rate constants to eq 1, are given in Table 4, not only for reactions **1** and **2**, but also for the backward reaction of **2**.

The reaction rate constants for reaction **2** as computed in the present work are 3−10 orders of magnitude smaller than those of Tabayashi and Bauer.[2] We also note that the calculated points are very well represented by the fits.

We can compare our computed reaction rate constants for reaction **1** ($CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$) with the accurate results obtained very recently for this reaction by Remmert et al. by means of a reduced dimensionality quantum dynamics study.[31] These authors compare their results with evaluated kinetic data of Kerr and Parsonage[70] as well as with those obtained by Kungwan and Truong[69] from canonical variational transition-state theory (CVT) including corrections for hindered rotation and tunneling. The latter correction was obtained using the multidimensional semiclassical small-curvature tunneling method (SCT) of Truhlar and co-workers.[71] Figure 2 shows that our computed rate constants for reaction **1** are slightly below those of Kerr and Parsonage.[70] This is consistent with the TST results reported by Remmert et al.[31] and Kungwan and Truong,[69] which also are slightly below the evaluated kinetic data of Kerr and Parsonage.[70] Remmert et al.[31] note that tunneling plays an important role in the low-temperature region. The tunneling correction obtained from the Wigner formula, however, is significantly smaller than the one obtained from the SCT method (see Table 3 and ref 69). At 600, 800, and 1000 K, for example, the SCT tunneling corrections are 1.7, 1.3, and 1.1 times larger than the Wigner values. Nevertheless, it was more the purpose of the present work to compute accurate reaction barrier heights than to compute accurate reaction rate constants. In this respect and, in particular, in view of the uncertainty in our tunneling corrections, the agreement between our computed rate constants and the experimental values for reaction **1** is satisfactory.

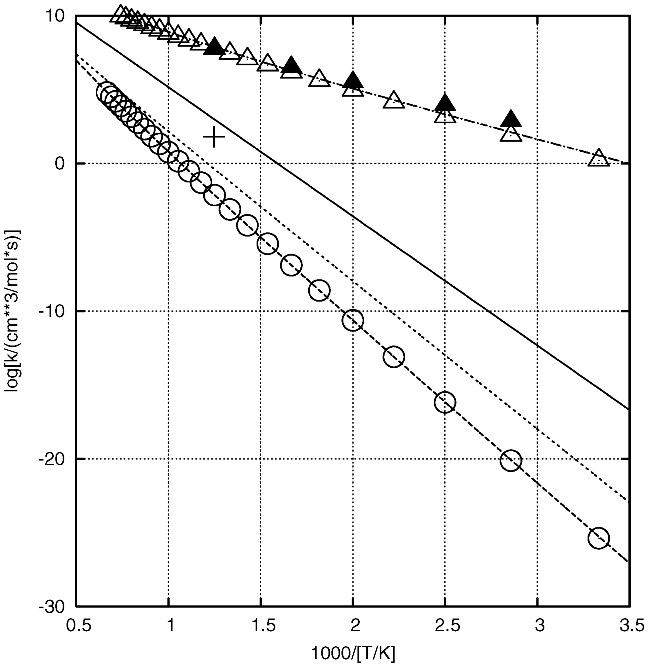

Figure 2. Reaction rate constants (k in cm^3 mol^{-1} s^{-1}) as a function of $1/T$ for the reactions $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ (Δ) and $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$ (○). For comparison, the rate constants used in ref 1 for the latter reaction are shown as a solid line. The upper limit of Back[5] at 802 K is marked as +. The rate constants of Skinner and Ruehrwein[4] are indicated as a dotted line. The evaluated experimental kinetic data of Kerr and Parsonage[70] for the reaction $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ are shown as ▲.

4. Conclusions

We have determined barrier heights of 71.8 ± 2.0 and 216.4 ± 2.0 kJ mol^{-1} for the reactions $CH_4 + CH_3^\bullet \rightarrow CH_3^\bullet + CH_4$ and $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$, respectively, from benchmark ab initio calculations. Using these barrier heights in conjunction with simple transition-state theory yields rate constants for the latter reaction that are orders of magnitude smaller than the ones used in the mechanism of ref 1 for the modeling of the pyrolysis of ethylene, acetylene, and propylene. Therefore, we suggest that it is necessary to reinvestigate the role of this reaction in that mechanism. Furthermore, we suggest using eq 1 with the parameters $A = 43$ cm^3 mol^{-1} s^{-1}, $n = 3.2$, and $E_a = 200$ kJ mol^{-1} for the reaction $CH_4 + CH_3^\bullet \rightarrow H^\bullet + C_2H_6$.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Projects KL 721/3-1 and TE 644/1-1. Additional support by DAAD (PROCOPE program) is gratefully acknowledged. We thank professors Olaf Deutschmann and Matthias Olzmann for comments on the manuscript and stimulating discussions.

References and Notes

(1) Norinaga, K.; Deutschmann, O. *Ind. Eng. Chem. Res.* **2007**, *46*, 3547.
(2) Tabayashi, K.; Bauer, S. H. *Combust. Flame* **1979**, *34*, 63.
(3) Kassel, L. S. *J. Am. Chem. Soc.* **1935**, *57*, 833.
(4) Skinner, G. B.; Ruehrwein, R. A. *J. Phys. Chem.* **1959**, *63*, 1736.
(5) Back, R. A. *Can. J. Chem.* **1983**, *61*, 916.
(6) Bachorz, R. A.; Hättig, C.; Klopper, W.; Tew, D. P. Unpublished.
(7) *Turbomole*, local experimental version of v5.10; Turbomole GmbH: Karlsruhe, January 2009. For the current public version, see: http://www.turbomole.com.
(8) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
(9) Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *94*, 4334.
(10) Fliegl, H.; Klopper, W.; Hättig, C. *J. Chem. Phys.* **2005**, *122*, 084107.
(11) Noga, J.; Kutzelnigg, W. *J. Chem. Phys.* **1994**, *101*, 7738.
(12) Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56.
(13) (a) Tew, D. P.; Klopper, W.; Neiss, C.; Hättig, C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1921. (b) Tew, D. P.; Klopper, W.; Neiss, C.; Hättig, C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6325; Erratum.
(14) Adler, T. B.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 221106.
(15) Noga, J.; Kedžuch, S.; Šimunek, J.; Ten-no, S. *J. Chem. Phys.* **2008**, *128*, 174103.
(16) Shiozaki, T.; Kamiya, M.; Hirata, S.; Valeev, E. F. *J. Chem. Phys.* **2008**, *129*, 071101.
(17) Köhn, A.; Richings, G. W.; Tew, D. P. *J. Chem. Phys.* **2008**, *129*, 201103.
(18) Valeev, E. F. *Phys. Chem. Chem. Phys.* **2008**, *10*, 106.
(19) Bokhan, D.; Ten-no, S.; Noga, J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3320.
(20) Torheyden, M.; Valeev, E. F. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3410.
(21) Bokhan, D.; Bernadotte, S.; Ten-no, S. *Chem. Phys. Lett.* **2009**, *469*, 214.
(22) Noga, J.; Šimunek, J. *Chem. Phys.* **2009**, *356*, 1.
(23) Shiozaki, T.; Kamiya, M.; Hirata, S.; Valeev, E. F. *J. Chem. Phys.* **2009**, *130*, 054101.

(24) Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.

(25) Köhn, A. *J. Chem. Phys.* **2009**, *130*, 131101.

(26) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(27) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1.

(28) For H, the aug-cc-pwCVTZ basis is identical to the aug-cc-pVTZ basis.

(29) Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J.; Auer, A. A.; Bernholdt, D. B.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Juselius, J.; Lauderdale, W. J.; Metzroth, T.; Michauk, C.; O'Neill, D. P.; Price, D. R.; Ruud, K.; Schiffmann, F.; Tajti, A.; Varner, M. E.; Vázquez, J. *ACES II*, (Mainz-Austin-Budapest 2005 version), a quantum chemical program package for high-level calculations of energies and properties, containing the integral packages *MOLECULE*; (Almlöf, J.; Taylor, P. R.), *PROPS*; (Taylor, P. R.), and *ABACUS*; (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), 2005; for the current version, see: http://www.cfour.de (*CFOUR* program).

(30) Layfield, J. P.; Owens, M. D.; Troya, D. *J. Chem. Phys.* **2008**, *128*, 194302.

(31) Remmert, S. M.; Banks, S. T.; Clary, D. C. *J. Phys. Chem. A* **2009**, *113*, 4255.

(32) (a) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041. (b) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3401; Erratum.

(33) Scuseria, G. E.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1988**, *152*, 382.

(34) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1990**, *93*, 6104.

(35) Bomble, Y. J.; Stanton, J. F.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 054101.

(36) Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 214105.

(37) Kállay, M. MRCC, a string-based quantum chemical program suite; http://www.mrcc.hu. Copy obtained on April 28, 2008.

(38) Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945.

(39) Peterson, K. A.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.

(40) Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190.

(41) Yousaf, K. E.; Peterson, K. A. *J. Chem. Phys.* **2008**, *129*, 184108.

(42) Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 4606.

(43) Hättig, C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59.

(44) Weigend, F. *J. Comput. Chem.* **2007**, *29*, 167.

(45) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(46) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(47) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(48) Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571.

(49) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model.* **2007**, *47*, 1045.

(50) Peterson Group Web site: http://tyr0.chem.wsu.edu/~kipeters/basissets/basis.html. Accessed November 2008.

(51) Tarczay, G.; Császár, A. G.; Klopper, W.; Quiney, H. M. *Mol. Phys.* **2001**, *99*, 1769.

(52) Coriani, S.; Helgaker, T.; Jørgensen, P.; Klopper, W. *J. Chem. Phys.* **2004**, *121*, 6591.

(53) Sansonetti, J. E.; Martin, W. C. *J. Phys. Chem. Ref. Data* **2005**, *34*, 1559; Also available at http://physics.nist.gov/PhysRefData/Handbook.

(54) McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, 1997.

(55) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*, 2nd ed.; Prentice Hall: New York, 1999.

(56) Strekalov, M. L. *Chem. Phys.* **2009**, *355*, 62.

(57) Aguilera-Iparraguirre, J.; Boese, A. D.; Klopper, W.; Ruscic, B. *Chem. Phys.* **2008**, *346*, 56.

(58) Klopper, W.; Ruscic, B.; Tew, D. P.; Bischoff, F. A.; Wolfsegger, S. *Chem. Phys.* **2009**, *356*, 14.

(59) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; von Laszewski, G.; Bittner, S.; Nijsure, S. G.; Amin, K. A.; Minkoff, M.; Wagner, A. F. *J. Phys. Chem. A* **2004**, *108*, 9979.

(60) Ruscic, B. Active Thermochemical Tables. *2005 Yearbook of Science and Technology*, annual update to McGraw-Hill Encyclopedia of Science and Technology; McGraw-Hill: New York, 2004.

(61) Ruscic, B.; Pinzon, R. E.; von Laszewski, G.; Kodeboyina, D.; Burcat, A.; Leahy, D.; Montoya, D.; Wagner, A. F. *J. Phys. Conf. Ser.* **2005**, *16*, 561.

(62) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; Srinivasan, N. K.; Su, M.-C.; Sutherland, J. W.; Michael, J. V. *J. Phys. Chem. A* **2006**, *110*, 6592.

(63) Schwenke, D. W. *Spectrochim. Acta, Part A* **1999**, *55*, 731.

(64) Schwenke, D. W. *Spectrochim. Acta, Part A* **2002**, *58*, 849.

(65) Karton, A.; Ruscic, B.; Martin, J. M. L. *J. Mol. Struct.: THEOCHEM* **2007**, *811*, 345.

(66) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(67) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

(68) Harding, M. E.; Vázquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2008**, *128*, 114111.

(69) Kungwan, N.; Truong, T. N. *J. Phys. Chem. A* **2005**, *109*, 7742.

(70) Kerr, J. A.; Parsonage, M. J. *Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals*; Butterworths: London, 1976.

(71) Truhlar, D. G.; Isaacson, A. D.; Skodje, R. T.; Garrett, B. C. *J. Phys. Chem.* **1982**, *86*, 2252.

JP902753S