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Thermochemistry of the Ethyl Radical and the C−H Bond Strength in Ethane

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CCSD(T) theory has been applied to the ethyl radical using aug-cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, and extrapolated to the complete basis set limit. QCISD/6-311G(d,p) results were used to estimate unknown frequencies in C_2H_5, and zero-point energies were combined with a correction for core electron correlation to find a 0 K bond dissociation enthalpy of 416.0 kJ mol^{-1} (422.5 kJ mol^{-1} at 298 K). This corresponds to $\Delta_f H(C_2H_5)$ values of 131.5 and 120.5 kJ mol^{-1} at 0 and 298 K, respectively. Uncertainties of ±2.1 kJ mol^{-1} are assumed.

1. Introduction

The thermochemistry of the ethyl radical establishes the carbon−hydrogen bond dissociation enthalpy (BDE) in ethane

$$C_2H_6 \rightarrow C_2H_5 + H \qquad (1)$$

through the relation

$$\mathrm{BDE} = \Delta_f H(H) + \Delta_f H(C_2H_5) - \Delta_f H(C_2H_6) \qquad (2)$$

The enthalpies of formation of H and C_2H_6 are well-defined. The strength of the simplest primary C−H bond is of fundamental importance to chemistry, and there have been several experimental determinations, some of which are listed in Table 1. There has been controversy surrounding some of the kinetic determinations. McMillen and Golden[1] selected a value based on the rate constant k_3 for

$$C_2H_6 + I \rightarrow C_2H_5 + HI \qquad (3)$$

combined with assumed parameters for the reverse rate constant k_{-3}. That value was called into question by the work of Tsang[2] and Pacey and Wimalasena[3] based on thermal decomposition of *n*-butane

$$n\text{-}C_4H_{10} \rightarrow 2\ C_2H_5 \qquad (4)$$

Cao and Back[4] considered the forward and reverse kinetics of the system

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \qquad (5)$$

and also recommended a more positive $\Delta_f H(C_2H_5)$. Hanning-Lee et al.[5] obtained the forward and reverse rate constants for the reaction

$$C_2H_4 + H \rightarrow C_2H_5 \qquad (6)$$

and thus the equilibrium constant $K_6 = k_6/k_{-6}$ as a function of temperature. Ruscic et al.[6] noted that some of these results were apparently inconsistent with the then current ionization potential (IP) of ethyl and value of $\Delta_f H(C_2H_5^+)$, and redetermined the IP to obtain $\Delta_f H(C_2H_5)$. Seakins et al.[7] and Nicovich et al.[8] investigated the kinetics of

$$C_2H_5 + HBr \rightarrow C_2H_6 + Br \qquad (7)$$

in both directions, and derived similar bond strengths via the equilibrium constant K_7. Recently, Dobis and Benson[9,10] have criticized those studies of reaction 7, and measured k_7 values about an order of magnitude smaller. As Dobis and Benson noted,[9] there is a similarly wide range in the literature values of k_{-7}, which allows for a significant range in K_7 and therefore $\Delta_f H(C_2H_5)$.

The aim of the present work is to obtain the C_2H_5−H bond strength via high-level ab initio calculations using coupled cluster theory with basis sets of up to quadruple-ζ quality, extrapolated to the complete basis set limit. The results permit an independent assessment of the experimental determinations.

2. Methodology

The BDE could in principle be obtained directly via the energy change for reaction 1. A more accurate result is expected from the isodesmic process

$$C_2H_6 + CH_3 \rightarrow C_2H_5 + CH_4 \qquad (8)$$

where, because the number and type of each bond are conserved, errors arising from basis set incompleteness and incomplete accounting of electron correlation mostly cancel. The geometry and frequencies of each species were first calculated at the QCISD/6-311G(d,p) level of theory. Next, the geometries and energies were obtained using CCSD(T) theory with three basis sets, aug-cc-pVDZ, cc-pVTZ, and cc-pVQZ.[11,12] Core electrons were excluded from the correlation treatments in all these calculations. To correct for this simplification, two energies at the final geometries were also obtained with a full double-ζ basis set augmented with polarization functions, D95(3df,2p),[13] where the core electrons were included and then excluded in the CCSD(T) calculations. All computations were made with the Gaussian 94 suite of programs.[14]

3. Results and Discussion

The computed geometries for C_2H_5 and C_2H_6 are summarized in Figure 1 and Table 2. By comparison with the equilibrium (r_e) structures for C_2H_2 and C_2H_4, Peterson and Dunning[15] found C−C and C−H bond length errors at the CCSD(T)/cc-pVQZ level of theory of around 0.003 Å (1 Å = 10^{-10} m), and an

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TABLE 1: Some Values of Ethyl Thermochemistry and the C_2H_5-H BDE[a]

Δ_fH_0	Δ_fH_{298}	BDE_0	BDE_{298}	method	ref
	108.4 ± 4.2		410.9 ± 4.2	$I + C_2H_6 \rightleftharpoons HI + C_2H_5$	1
	119 ± 2			$n\text{-}C_4H_{10} \rightleftharpoons 2\ C_2H_5$	2,3
	117			$H + C_2H_6 \rightleftharpoons H_2 + C_2H_5$	4
	120.2 ± 0.9			$H + C_2H_4 \rightleftharpoons C_2H_5$	5
132.2 ± 2.4		416.6 ± 2.4		$C_2H_5 \rightarrow C_2H_5^+$	6
	121.9 ± 1.8			$HBr + C_2H_5 \rightleftharpoons Br + C_2H_6$	7
	121.8 ± 2.1		423.8 ± 2.5	$HBr + C_2H_5 \rightleftharpoons Br + C_2H_6$	8
	118.8 ± 1.0		420.5 ± 1.3	$HBr + C_2H_5 \rightleftharpoons Br + C_2H_6$	9
131.5 ± 2.1	120.5 ± 2.1	416.0 ± 2.1	422.5 ± 2.1	CCSD(T) theory	this work

[a] In kJ mol^{-1}.

TABLE 2: CCSD(T) Geometries of C_2H_5 and C_2H_6[a]

	ethyl (C_s symmetry)			ethane (D_{3d} symmetry)		
parameter	aug-cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	cc-pVTZ	cc-pVQZ
CH_a[b]	1.112	1.099	1.098	1.106	1.092	1.091
CH_b[b]	1.106	1.092	1.091			
CH_c[b]	1.095	1.081	1.080			
CC[b]	1.506	1.492	1.489	1.540	1.529	1.526
CCH_a[c]	111.60	111.67	111.63	111.15	111.20	111.21
CCH_b[c]	111.44	111.52	111.57			
CCH_c[c]	120.78	120.74	120.80			
H_bCCH_a[d]	±119.42	±119.42	±119.36			
H_cCCH_a[d]	±85.06	±85.00	±85.44[e]			

[a] Atom labeling defined in Figure 1. [b] Bond length in 10^{-10} m. [c] Bond angle in degrees. [d] Dihedral angle in degrees. [e] Convergence to 0.5° accepted for this parameter, rather than default of 0.1°.

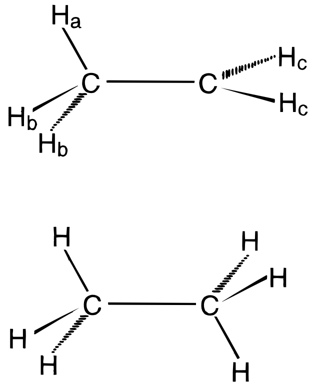

Figure 1. Structures of ethyl (C_s) and ethane (D_{3d}). Parameters given in Table 2.

TABLE 3: QCISD/6-311G(d,p) Frequencies (in cm^{-1}) for Ethyl and Ethane, Scaled by 0.956

C_2H_5	symmetry	C_2H_6	symmetry
145	A″	311	A_{1u}
435	A′	795 (2)[a]	E_u
780	A″	981	A_{1g}
958	A′	1189 (2)	E_g
1030	A′	1364	A_{2u}
1161	A″	1392	A_{1g}
1362	A′	1455 (2)	E_g
1426	A′	1459 (2)	E_u
1440	A′	2918	A_{2u}
1442	A″	2921	A_{1g}
2871	A′	2976 (2)	E_g
2946	A′	2998 (2)	E_u
2987	A″		
3026	A′		
3124	A″		

[a] Doubly degenerate.

error of 0.03° in the ethylene HCH angle. Presumably similar uncertainties apply here.

Frequency information is given in Table 3. Where available, experimental fundamental frequencies ν_0 were employed to calculate vibrational zero-point energy contributions. All the C_2H_6 modes are known,[16] but in the case of C_2H_5, three of the 15 normal modes have not been observed.[17] Figure 2 is a plot of experimental versus QCISD/6-311G(d,p) frequencies of ethyl, which have been discussed previously,[18,19] and ethane, together with a linear fit constrained to pass through the origin. The root-mean-square deviation is 39 cm^{-1} and the slope is 0.956. This scale factor, which mainly accounts for anharmonicity, was used here to predict ν_0 for the three missing modes for ethyl, at 145 (torsion), 780, and 1426 cm^{-1}.

Although the thermochemical tables of Gurvich et al.[16] for C_2H_5 are based on a significant torsional barrier, there is evidence that the barrier is small. Cohen[20] used 0.71 kJ mol^{-1}, Suter and Ha[21] obtained a zero-point energy corrected value of 0.31 kJ mol^{-1} from MP2/6-31G(d,p) theory, East and Bunker[22] found the same value from MP2/cc-pVTZ theory, and Tirtowidjojo et al.[10] derived 0.56 kJ mol^{-1} from fitting a sinusoidal potential to the QCISD/6-311G(d,p) harmonic frequency. In this work, QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) calculations at the minimum energy geometry and the transition state for internal rotation yield an electronic energy barrier of 0.30 kJ mol^{-1}. This falls to only 0.08 kJ mol^{-1} after correcting for changes in zero-point energy. Recent high-resolution IR spectroscopy measurements[23] are consistent with a low rotational barrier, between 0.1 and 0.5 kJ mol^{-1}. For the purpose of calculating the temperature dependence of the enthalpy of ethyl, its torsion is therefore treated as free, with a symmetry number of 6 and a reduced moment of inertia, based on the CCSD(T)/cc-pVQZ geometry, of 2.10×10^{-47} kg m^2. With use of the rigid rotor/harmonic oscillator approximation for the other motions of C_2H_5, $H_{298.15}-H_0$ is calculated to be 12.18 kJ mol^{-1}, which lies between the Gurvich et al.[16] value of 11.81 kJ mol^{-1} and the Thermodynamics Research Center tabulation of 12.30 kJ mol^{-1}.[24] On the same basis, the entropy $S_{298.15}$ is found to be 247.7 J K^{-1} mol^{-1}, which falls between the values employed by Nicovich et al.[8] and Dobis and Benson,[9] of 246.8 and 249.4 J K^{-1} mol^{-1}, respectively.

The ab initio energies are listed in Table 4 and are used to

TABLE 4: Energies for Species in the Reaction $C_2H_6 + CH_3 \rightarrow C_2H_5 + CH_4$[a]

calculation	$C_2H_6(^1A_{1g})$/au	$CH_3(^2A_2'')$/au	$C_2H_5(^2A')$ /au	$CH_4(^1A_1)$/au	ΔE/kJ mol^{-1}
CCSD(T)/aug-cc-pVDZ	−79.597 970	−39.724 710	−78.931 486	−40.395 820	−12.15
CCSD(T)/cc-pVTZ	−79.674 445	−39.760 976	−79.002 506	−40.438 099	−13.61
CCSD(T)/cc-pVQZ	−79.698 718	−39.772 449	−79.025 724	−40.450 888	−14.30
CBS limit[b]					−14.90
CCSD(T)=full/D95(3df,2p)	−79.686 040	−39.765 936	−79.015 700	−40.442 112	−15.32
CCSD(T)=fc/D95(3df,2p)	−79.649 064	−39.748 112	−78.979 223	−40.423 535	−14.66
ZPE[c]	0.072 283	0.028 990	0.057 629	0.043 224	−1.10
ΔH_0					−16.67

[a] In au, 1 au ≈ 2625.3 kJ mol^{-1}. [b] Complete basis set limit. [c] Zero-point energy.

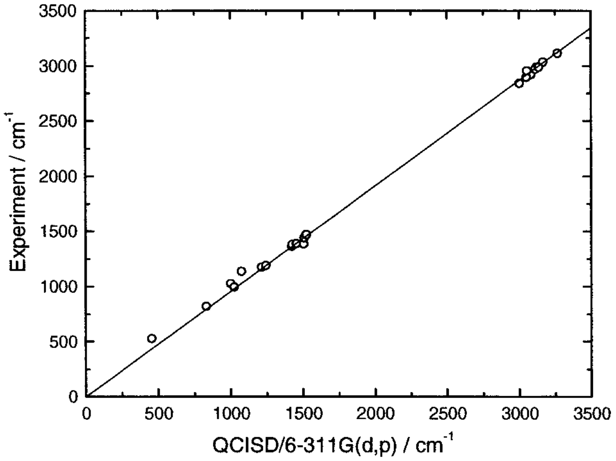

Figure 2. Comparison of calculated harmonic QCISD/6-311G(d,p) and observed fundamental vibrational frequencies for ethyl and ethane.

derive the energy change ΔE for reaction 8 at various levels of theory. The complete basis set limit was obtained by fitting the CCSD(T)/cc-pVnZ values to the functional form $\Delta E = \Delta E_\infty + A \exp(-Bn)$ and extrapolating to infinite n, i.e., to ΔE_∞.[25] Two corrections were applied to this extrapolated ΔE. The first was for the neglect of core correlation, equal to ΔE[CCSD(T)=full]$-\Delta E$[CCSD(T)=fc] with the D95(3df,2p) basis set, which came to −0.67 kJ mol^{-1}. The second correction was for changes in vibrational zero-point energy, here set equal to $^1/_2\ \Sigma h\nu_0$ where ν_0 is obtained from the experimental fundamental frequencies (except for the three missing modes for C_2H_5 discussed above). After these corrections, ΔE equals ΔH_0 for reaction 8, where

$$\Delta H_0 = \mathrm{BDE}_0(C_2H_5{-}H) - \mathrm{BDE}_0(CH_3{-}H) \qquad (8)$$

Litorja and Ruscic[26] have recently measured $\mathrm{BDE}_0(CH_3{-}H)$ to high precision, 432.64 ± 0.29 kJ mol^{-1}; hence $\mathrm{BDE}_0(C_2H_5{-}H) = 415.96$ kJ mol^{-1} is obtained. The present value of $H_{298.15}-H_0$ for C_2H_5 and tabulated values[16,27] for C_2H_6 and H of 11.88 and 6.20 kJ mol^{-1} imply $\mathrm{BDE}_{298.15}(C_2H_5{-}H) = 422.46$ kJ mol^{-1}. These bond dissociation enthalpies can be combined with the enthalpies of formation of C_2H_6 and H, −68.38 and 216.04 kJ mol^{-1} at 0 K and −84.00 and 218.00 kJ mol^{-1} at 298.15 K, respectively,[16,27] using eq 2, to find the $\Delta_f H(C_2H_5)$ values listed in Table 1.

The least certain input parameter is $\Delta_f H(C_2H_6)$ but the quoted uncertainty is only ±0.4 kJ mol^{-1}.[16] An earlier recommendation is 0.75 kJ mol^{-1} more negative.[28] Because the zero-point energies mostly cancel for reaction 8, uncertainties in frequencies have little influence. Because the ΔE for reaction 8 is close to converged, the basis set extrapolation introduces little uncertainty: use of an alternative formula[25] $\Delta E = \Delta E_\infty + A/(l + {}^1/_2)^4 + B/(l + {}^1/_2)^6$ (where l is the highest angular momentum function, 2, 3, and 4 here) leads to $\Delta E_\infty = -14.81$ kJ mol^{-1} instead. In order to estimate the reliability of the derived $\Delta_f H(C_2H_5)$ values, it is noted that, using a similar computational approach applied to BDEs in the series CH_n and C_2H_n ($n \leq 4$), Peterson and Dunning[15] found errors of up to 0.8 and 1.7 kJ mol^{-1}, respectively, by comparison with experiment. They expected accuracies of 2.1 kJ mol^{-1} for two unknown C_2H_n BDEs, and this same error limit is used here. This may be somewhat pessimistic: the earlier work[15] was not able to take advantage of the cancellations in isodesmic reactions, and there were changes in the C−C bond order.

The thermochemistry for reaction 8 can be compared to results from the Gaussian-x series of model chemistries. Ruscic et al.[6] reported $\Delta H_0 = -13.0$ kJ mol^{-1} from G1 theory. Use of G2 energies[29] in reaction 8 yields $\Delta H_0 = -13.7$ kJ mol^{-1}, and G3 data[30,31] imply $\Delta H_0 = -12.9$ kJ mol^{-1}. The last calculation includes core electron correlation, like the present work. Those results are around 3−4 kJ mol^{-1} more positive than our best calculation and would therefore lead to a similar deviation in $\Delta_f H(C_2H_5)$. We are applying G*x* methods to the thermochemistry of larger alkyl radicals and the present results provide a calibration of the derived bond strengths.

Our computed thermochemistry may also be compared to the various experimental results in Table 1. Clearly it supports the newer measurements which are more positive than the results from iodination kinetics. There is accord within the uncertainty with the results of *n*-butane dissociation, and exceptionally close agreement with the results based on ionization of ethyl and on the kinetics of dissociation of ethyl radicals (combined with the reverse process, addition of H atoms to ethylene), to within 0.7 kJ mol^{-1}. The deviation of 3.5 kJ mol^{-1} from the value based on $H + C_2H_6$ kinetics suggests there might be some moderate but unresolved discrepancies between forward and reverse rate constants in that system. The present results lie within the small range of thermochemistry based on $HBr + C_2H_5 \rightleftharpoons Br + C_2H_6$ kinetics. However, the narrowness of this range is fortuitous, because of the wide disparities in forward and reverse rate constants noted in the Introduction. Different selections lead to different equilibrium constants and a range of over 11 kJ mol^{-1} in the derived $\Delta_f H(C_2H_5)$.[9] The present work does not determine the rate constants, but does fix their ratio. In combination with tabulated data for the other reactants,[16,27] our thermochemical data for C_2H_5 implies $K_7 = 4.6 \times 10^7$ at 298 K. This is rather close to the value of $(5.1 \pm 2.5) \times 10^7$ derived[9] from flash photolysis measurements of k_7 and k_{-7}.[7,8] The uncertainty assumed in $\Delta_f H(C_2H_5)$ implies about a factor of 2 uncertainty in the present K_7 at 298 K, which therefore accommodates some of the k_7 and k_{-7} results from VLPP and thermal measurements that yielded K_7 in the range $(1.2{-}3.0) \times 10^7$.[9] With our computed K_7, if an unambiguous determination of k_7 or k_{-7} can be made, then much of the uncertainty in the remaining quantity will also be resolved.

Conclusions

Coupled cluster theory has been combined with extrapolation of correlation consistent basis sets and a core electron correction to obtain the C_2H_5-H bond dissociation enthalpy at the complete basis set limit. The value is in good accord with several recent experiments, and constrains the ratio of forward and reverse kinetics for the Br + C_2H_6 system. The barrier to internal rotation in ethyl is found to be negligible, about 0.1 kJ mol^{-1}.

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