J. Phys. Chem. A **2007,** *111,* 113−126 **113**

Theoretical Prediction of the Heats of Formation of $C_2H_5O^•$ Radicals Derived from Ethanol and of the Kinetics of *β*-C−C Scission in the Ethoxy Radical

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Received: June 29, 2006; In Final Form: October 25, 2006

Thermochemical parameters of three $C_2H_5O^•$ radicals derived from ethanol were reevaluated using coupled-cluster theory CCSD(T) calculations, with the aug-cc-pV*n*Z (n = D, T, Q) basis sets, that allow the CC energies to be extrapolated at the CBS limit. Theoretical results obtained for methanol and two $CH_3O^•$ radicals were found to agree within ±0.5 kcal/mol with the experiment values. A set of consistent values was determined for ethanol and its radicals: (a) heats of formation (298 K) $\Delta H_f(C_2H_5OH) = -56.4 \pm 0.8$ kcal/mol (exptl: -56.21 ± 0.12 kcal/mol), $\Delta H_f(CH_3C^•HOH) = -13.1 \pm 0.8$ kcal/mol, $\Delta H_f(C^•H_2CH_2OH) = -6.2 \pm 0.8$ kcal/mol, and $\Delta H_f(CH_3CH_2O^•) = -2.7 \pm 0.8$ kcal/mol; (b) bond dissociation energies (BDEs) of ethanol (0 K) BDE($CH_3CHOH-H$) = 93.9 ± 0.8 kcal/mol, BDE(CH_2CH_2OH-H) = 100.6 ± 0.8 kcal/mol, and BDE(CH_3CH_2O-H) = 104.5 ± 0.8 kcal/mol. The present results support the experimental ionization energies and electron affinities of the radicals, and appearance energy of (CH_3CHOH^+) cation. *β*-C−C bond scission in the ethoxy radical, $CH_3CH_2O^•$, leading to the formation of $C^•H_3$ and $CH_2{=}O$, is characterized by a C−C bond energy of 9.6 kcal/mol at 0 K, a zero-point-corrected energy barrier of $E_0^‡ = 17.2$ kcal/mol, an activation energy of $E_a = 18.0$ kcal/mol and a high-pressure thermal rate coefficient of $k_\infty(298\ K) = 3.9\ s^{-1}$, including a tunneling correction. The latter value is in excellent agreement with the value of 5.2 s^{-1} from the most recent experimental kinetic data. Using RRKM theory, we obtain a general rate expression of $k(T,p) = 1.26 \times 10^9 p^{0.793} \exp(-15.5/RT)\ s^{-1}$ in the temperature range (T) from 198 to 1998 K and pressure range (p) from 0.1 to 8360.1 Torr with N_2 as the collision partners, where $k(298\ K, 760\ Torr) = 2.7\ s^{-1}$, without tunneling and $k = 3.2\ s^{-1}$ with the tunneling correction. Evidence is provided that heavy atom tunneling can play a role in the rate constant for *β*-C−C bond scission in alkoxy radicals.

Introduction

Ethanol is an important fuel additive for internal combustion engines and can play a role in developing energy independence as well as in reducing green house gas emissions.[1] It has been estimated that the use of ethanol produced from corn could reduce CO_2 emissions by 10−15% as compared to use of gasoline as a fuel.[2] Ethanol is an important component of the ethanol-based E-diesel fuel currently used in fleet vehicles as well as in some alternative biofuels.[3] Currently, ethanol constitutes 99% of all of the biofuels used in the USA.[3] As a consequence of the recent U.S. Energy Policy Act (EPACT 2005), the use of ethanol as a motor fuel is expected to be greatly increased as there is a mandate for up to 7.5 billion gallons of "renewable fuel" to be used in gasoline by 2012.

In view of the importance of ethanol as a fuel for internal combustion engines, thermochemical and kinetic parameters for its oxidation reactions have been obtained from both experimental and theoretical studies. The initial steps in the combustion of ethanol involve loss of a hydrogen atom. The three unique radicals that can be formed are $CH_3C^•HOH$ (**1**), $C^•H_2CH_2OH$ (**2**), and $CH_3CH_2O^•$ (**3**). In addition, the tropospheric degradation of ethanol will proceed by hydrogen abstraction by the OH radical. In general, for $R-H + X^•$ reactions, the radical product channel with the highest exothermicity (lowest R−H bond energy) has the highest rate constant under atmospheric conditions.[4,5] The *β*-hydroxyethyl radical **2** is the primary initial radical formed in the tropospheric oxidation of ethane. The ethoxy radical **3** is also involved in the atmospheric oxidation process of ethane, in the presence of NO_x as described in eq 1.

$$C_2H_6 \xrightarrow{-H} C_2H_5^• \xrightarrow{+O_2} C_2H_5O_2^• \xrightarrow{+NO} C_2H_5O^• + NO_2 \quad (1)$$

The radical **3** is the prototype for the decomposition of the important class of alkoxy radicals. Although the formation enthalpies of the resulting free radicals **1**, **2**, and **3**, and the corresponding C−H and O−H bond dissociation energies (BDEs) of ethanol, are of crucial importance in evaluating reaction product distributions, they have not been determined with high accuracy yet. This is not surprising in view of the fact that for the homologues derived from methanol ($C^•H_2OH$ and $CH_3O^•$), no less than one hundred papers have been devoted to their thermochemical properties before a consensus could be reached.[6]

We first summarize the available experimental results on $C_2H_5O^•$ radicals (see Table 1) to put our work in context. In 1962, Whittle and co-workers[7] studied the BDEs of alcohols and established that, in ethanol, the homolytic bond breaking occurs at the α-carbon, with BDE($CH_3CHOH-H$) ≤ 92 kcal/mol, giving rise to **1**. Walsh and Benson[8] subsequently derived a larger value, BDE = 95 kcal/mol. Alfassi and Golden[9] investigated the kinetics of the reaction of iodine atom with

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10.1021/jp064086f CCC: $37.00

TABLE 1: Summary of Experimental and Theoretical Heats of Formation (ΔH_f) of ($C_2H_5O^•$) Radicals and Bond Dissociation Energies (BDE) of Ethanol[a]

		$CH_3C^•HOH$		$C^•H_2CH_2OH$		$CH_3CH_2O^•$		
year	method	ΔH_f	BDE	ΔH_f	BDE	ΔH_f	BDE	ref
1962	photobromination		≤92					7
1964	iodine reaction		95					8
1972	iodine reaction	−15.2 ± 1.0 [−12.0]	93.0 ± 1.0 [91.5]					5, 9
1982	mass spectrometry			−2.5		4.1		10
1982	photoelectron					−6 ± 2		13
1987	MP4SDQ/6-31G(*d*,*p*)	[−11.6]		−7.5 [−5.1]				24
1990	photoelectron					−3.6 ± 0.8 y[−0.4 ± 0.9]	104.3 ± 1.0 [103.1 ± 1.0]	5, 16
1991	appearance energy	−14.5 ± 3		−13.5 ± 3				14
1994	photoionization	−13.7 ± 2 [−10.5 ± 2]	94.5 ± 2 [93 ± 2]	−8.7 ± 2 [−5.5 ± 2]	99.5 ± 2 [98 ± 2]			15
1995	G2	−12.9 [−9.7]	[94.9]	−5.9 [−2.7]	[101.9]	−3.1 [0.1]	[104.6]	25
1997	laser-induced fluorescence			−7.5 ± 1.7				5, 21
1997	photoelectron	−13.6 ± 0.9	94.5 ± 0.9					17
1997	MP4, QCISD(T) and CCSD(T)			−4.0 ± 1.0				26
1999	CBS-Q			−8.0		−1.7		27
2001	CBS-Q						[105.0]	28
2002	gas phase acidity					−3.6 ± 0.8	104.7 ± 0.8 [103.5 ± 0.8]	18, 29
2003	CBS-RAD					−2.37 [1.0]		30
2005	IUPAC evaluation					−3.25 ± 1.0 [−0.05 ± 1.0]		22
2006	ccCA					−2.3		32

[a] Values at 298 K in kcal/mol. Values at 0 K are given in brackets.

ethanol, and from the measured activation energy and an assumption about the reverse reaction, these authors[9] obtained BDE = 93.0 ± 1.0 kcal/mol, and $\Delta H^0_{f,298}(\mathbf{1}) = -15.2 \pm 1.0$ kcal/mol. These values were used in literature compilations.[10,11] In the 1982 review,[10] the corresponding $\Delta H^0_{f,,298}$ values for the two isomeric radicals were also given, $\Delta H^0_{f,298}(\mathbf{2}) = -2.5$ kcal/mol and $\Delta H^0_{f,298}(\mathbf{3}) = 4.1$ kcal/mol (very similar values for **1**, **2**, and **3** are also found in ref 12). On the basis of photoelectron spectroscopy experiments of the corresponding alkoxide, Ellison et al.[13] derived a value of $\Delta H^0_{f,298}(\mathbf{3}) = -6 \pm 2$ kcal/mol. Holmes et al.[14] obtained from appearance energy measurements by mass spectrometry, $\Delta H^0_{f,298}(\mathbf{1}) = -14.5 \pm 3$ kcal/mol and $\Delta H^0_{f,298}(\mathbf{2}) = -13.5 \pm 3$ kcal/mol. Although the earlier energy ordering between both isomers was confirmed, the energy gap was markedly reduced. Ruscic and Berkowitz[15] reported in 1994 using photoionization mass spectrometry, the most complete set of ethanol BDEs as well as various thermochemical parameters of the ($C_2H_5O^+$) cation isomers, including the proton affinity of acetaldehyde. It is worth noting that the α-hydroxyethyl radical **1** can be formed by electron attachment to protonated acetaldehyde. These authors[15] derived the energies for both α(C−H) and β(C−H) bonds, $BDE_{298}(CH_3CHOH-H) \sim 94.5$ kcal/mol (∼93 kcal/mol at 0 K), and $BDE_{298}(CH_2CH_2OH-H) = 99.5 \pm 2$ kcal/mol (98 ± 2 kcal/mol at 0 K). The formation enthalpies of the corresponding free radicals were evaluated as $\Delta H^0_{f,298}(\mathbf{1}) = -13.7$ kcal/mol, $\Delta H^0_{f,0}(\mathbf{1}) = -10.5$ kcal/mol, $\Delta H^0_{f,298}(\mathbf{2}) = -8.7 \pm 2$ kcal/mol, and $\Delta H^0_{f,0}(\mathbf{2}) = -5.5 \pm 2$ kcal/mol. There are significant differences with respect to the earlier experimental values. For **1**, Ruscic and Berkowitz[15] stated that the 1972 value reported by Alfassi and Golden[9] is about 1−3 kcal/mol too negative. Whereas Holmes et al.[14] estimated an energy difference of only 1 kcal/mol between **1** and **2**, Ruscic and Berkowitz[15] derived a larger gap of 5 kcal/mol. Ervin et al.[16] redetermined the absolute gas phase acidities (GA) of alcohols including ethanol, $\Delta G_{acid,298}(CH_3CH_2O-H) = 372.0 \pm 0.6$ kcal/mol. Together with the electron affinity of the ethoxy radical,[13] EA(**3**) = 1.726 ± 0.033 eV, $BDE_{298}(CH_3CH_2O-H) = 104.3 \pm 1.0$ kcal/mol was derived, which corresponds to $BDE_0(CH_3CH_2O-H) = 103.1 \pm 1.0$ kcal/mol. The 298 K value is similar to that of methanol, $BDE_{298}(CH_3O-H) = 104.1 \pm 0.5$ kcal/mol, obtained using the same approach. These results led to $\Delta H^0_{f,298}(\mathbf{3}) = -3.6 \pm 0.8$ kcal/mol and $\Delta H^0_{f,0}(\mathbf{3}) = -0.4 \pm 0.9$ kcal/mol. There is a difference of 7.8 kcal/mol between the kinetic and GA-derived values for the standard formation enthalpy of **3**. Dyke et al.[17] recorded the He I photoelectron spectra for CH_3CHOH (**1**) as the product from the F + C_2H_5OH reaction. The first adiabatic ionization energy of **1** is $IE_a(\mathbf{1}) = 6.64 \pm 0.3$ eV. These authors derived $\Delta H^0_{f,298}(\mathbf{1}) = -13.6 \pm 0.9$ kcal/mol and $BDE_{298}(CH_3CHOH-H) = 94.5 \pm 0.9$ kcal/mol, close to values reported in ref 15. DeTuri and Ervin[18] subsequently revised the gas phase acidity of ethanol as $\Delta G_{acid,298}(CH_3CH_2O-H) = 372.6 \pm 1.2$ kcal/mol and obtained $BDE_{298}(CH_3CH_2O-H) = 105.2 \pm 1.2$ kcal/mol and $\Delta H^0_{f,298}(\mathbf{3}) = -3.3 \pm 1.2$ kcal/mol.

The recent summary of the evaluated experimental values from the NASA Stratospheric Modeling Data Panel[5] gave the following values $\Delta H^0_{f,298}(\mathbf{3}) = -3.7 \pm 0.8$,[19] $\Delta H^0_{f,298}(\mathbf{1}) = -15.2 \pm 1$,[20] and $\Delta H^0_{f,298}(\mathbf{2}) = -7.5 \pm 1.7$ kcal/mol.[21] In the recent IUPAC critical compilation of thermochemical properties of radicals,[22] the values determined from gas phase acidity measurements by DeTuri and Ervin[18] and the more recent electron affinity value[23] for CH_3CH_2O were used to establish the following results for the ethoxy radical, $\Delta H^0_{f,0}(\mathbf{3}) = -0.05 \pm 1.0$ kcal/mol and $\Delta H^0_{f,298}(\mathbf{3}) = -3.25 \pm 1.0$ kcal/mol. The latter value is consistent within the reported error bars of the NASA Panel value.

There have been a number of computational studies of the heats of formation and BDEs as well. At the (P)UMP4/6-31G(d) molecular orbital theory level, Sosa and Schlegel[24] obtained a theoretical estimate of $\Delta H^0_{f,298}(\mathbf{2}) = -7.5$ kcal/mol, based

TABLE 2: Calculated Atomization Energies (in kcal/mol).

molecule	CBS[a]	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	ΣD_0(0 K)
CH_3OH ($^1A'$)[f]	512.28	−31.57	1.27	−0.52	−0.308	481.16
CH_3OH^+ ($^2A''$)[g]	258.44	−28.86	1.10	−0.43	−0.308	229.94
CH_2OH (^2A)	408.90	−23.21	1.23	−0.50	−0.308	386.11
CH_2OH^+ ($^1A'$)[h]	237.23	−24.86	1.04	−0.47	−0.308	212.63
CH_3O ($^2A'$)	399.11	−23.09	1.15	−0.38	−0.308	376.49
H_3CO^- ($^1A_1$)	434.89	−22.16	1.08	−0.50	−0.308	413.01
H_3CO^+ ($^3A_1$)	149.98	−20.61	1.12	−0.24	−0.308	129.93
CH_3CH_2OH ($^1A'$)[f]	808.86	−49.25	2.36	−0.74	−0.393	760.83
$CH_3C^{\bullet}HOH$ (**1**,$^1A'$)	706.87	−41.18	2.34	−0.71	−0.393	666.93
$C^{\bullet}H_2CH_2OH$ (**2**,^2A)	699.32	−40.22	2.25	−0.70	−0.393	660.25
$CH_3CH_2O^{\bullet}$ (**3,** $^2A'$)[i]	694.99	−40.91	2.17	−0.62	−0.393	655.24
$CH_3CH_2O^{\bullet}$(**3,**$^2A''$)[i]	695.47	−40.32[j]	2.21	−0.62	−0.393	656.35
$CH_3CH_2O^{\bullet}$ (**3-TS**, $^2A'$)[i]	675.94	−37.88	2.09	−0.63	−0.393	639.13
$CH_3CH_2OH^+$ ($^2A''$)[j]	562.95	−46.21	2.17	−0.63	−0.393	517.88
CH_3CHOH^+ ($^1A'$)[h]	552.70	−42.44	2.19	−0.68	−0.393	511.38
$CH_2CH_2OH^-$ (^1A)	713.52	−39.25	2.19	−0.73	−0.393	675.34
$CH_3CH_2O^-$ ($^1A'$)	734.69	−40.11	2.12	−0.72	−0.393	695.59

[a] From CCSD(T)/CBS energies extrapolated using eq 5, with aV*n*Z basis sets, where n = D, T and Q, based on at the MP2/aVTZ optimized geometries, unless otherwise noted. Total energies are given Table S1 (Supporting Information). [b] Calculated zero-point energies are reported in Table S4 (Supporting Information). A scaling factor of 0.977 obtained from methanol was applied to its radicals and ions, and 0.980 obtained from ethanol was applied to its corresponding radicals and ions, unless otherwise noted. [c] Core/valence corrections were obtained with the cc-pwCVTZ basis sets. [d] The scalar relativistic correction (MVD) is from a CISD/aVTZ calculation. [e] Values obtained from ref 57. [f] Geometry at MP2/aVTZ, and ZPE averaged from CCSD(T)/aVDZ and experiment. [g] UCCSD(T)/aVDZ optimized geometries. ZPE's were evaluated from UCCSD(T) harmonic vibrational frequencies and scaled by 0.985. [h] Values taken from ref 45. [i] Geometries at UCCSD(T)/aVTZ, and ZPE from UCCSD(T)/aVDZ frequencies, scaled by 0.988. [j] UCCSD(T)/aVDZ optimized geometries. ZPE's were evaluated from UCCSD(T) harmonic vibrational frequencies and scaled by 0.988.

on two different evaluation strategies. Curtiss et al.[25] reported a G2 value of $\Delta H^0_{f,298}$(**2**) = −5.9 kcal/mol. Espinosa-García[26] subsequently carried out a careful reevaluation by using four distinct working chemical reactions and five different levels of MO theory, and proposed a value of $\Delta H^0_{f,298}$(**2**) = −4.0 ± 1.0 kcal/mol. For this quantity, Yamada et al.[27] calculated a value of $\Delta H^0_{f,298}$(**2**) = −8.0 kcal/mol using CBS-q//MP2(full)/6-31G(d,p) and G2 methods. In view of the substantial differences (cf. experimental values of −13.5[14] and −8.7[15] kcal/mol), these authors[27] called for "further studies to clarify this value". Sumathi et al.[28] obtained using CBS-Q calculations a value of BDE(C_2H_5O−H) = 105.0 kcal/mol, which is close to the G2 value. On the basis of previous experimental and theoretical studies, Erwin and DeTuri[29] proposed a value of −3.6 kcal/mol for ΔH^0_f(**3**) at 298 K. Rauk et al.[30] reported values of +1.0 and −2.37 kcal/mol for ΔH^0_f(**3**) at 0 and 298 K, respectively, using the CBS-RAD approach. Lin and co-workers[31] used the G2M(RCC2) method and determined energy differences of 11.9 and 3.8 kcal/mol for the pairs **2**−**1** and **3**−**2**, respectively. More recently, DeYonker et al.[32] used the new correlation consistent composite approach (ccCA) to obtain ΔH^0_f(**3**) at 298 K of −2.3 kcal/mol.

Two potential low-energy channels are possible for the unimolecular decomposition of **3**: β-C−C bond scission forming methyl and formaldehyde and loss of an α-H to form acetaldehyde. We consider the former channel, which is the lowest energy one and most likely.[30] Unless otherwise noted, the results stated hereafter refer to β-C−C bond scission. The earlier kinetic results for the decomposition of alkoxy radicals in the gas phase have been reviewed by Batt.[33a] The activation energy (E_a) for β-C−C bond scission in **3** are dependent on the experimental conditions. The values are clearly not in agreement with low values of 12.5 kcal/mol (10−30 Torr of pressure[33b]) and 13.0 kcal/mol (5−30 Torr[33c]) and a much higher value of 22.1 kcal/mol (50 Torr[33d]). Hoyermann et al.[34] summarized the high-pressure limit Arrhenius parameters and concluded that E_a is in the range 20.2−21.6 kcal/mol with log(A) ranging from 13.7 to 15.0. These authors also carried out calculations at the UMP2/6-31G(d) level for the geometries and vibrational frequencies, UMP2/6-311+G(d,p) for the energies and obtained an energy barrier of 20.85 kcal/mol, which led to E_a = 22.0 kcal/mol and log(A) = 13.9 at 400 K.[34] Caralp et al.[35] performed a kinetic study to determine thermal rate constants. Within the pressure range $0.001 < p < 60$ bar of He, and temperature range $391 < T < 471$ K, a high-pressure rate expression was derived as $k_\infty = 1.1 \times 10^{13} \exp(-16.8/RT)$ s^{-1} (reported E_a = 70.3 kJ mol^{-1}) giving a derived rate of k_∞ (298 K) = 5.2 s^{-1}. These authors also performed ab initio calculations showing that activation parameters obtained by different levels of theory markedly deviate from each other (cf. Table 2 of ref 35). The best levels used in this study, QCISD(T)[36] with the 6-311+G(3df,2p) basis set and BAC-MP4,[37] gave respective zero-point-corrected barrier heights, $E_0^{\ddagger}$, of 16.9 and 17.4 kcal/mol, and respective k_∞(400 K) = 9.6 and 5.9 s^{-1}.[35] The C−C bond dissociation energy was calculated to be 9.5 kcal/mol at 298 K. A theoretical study by Yamada et al.[27] did not agree well with the most recent experimental results of Hoyerman et al.[34] Yamada et al. predicted $E_0^{\ddagger}$'s of 13.4 and 16.0 kcal/mol at 298 K from CBS-q[38] and G2[39] calculations, respectively. From their high-pressure rate expression with the CBS-q barrier height,[27] one obtains k_∞(296 K) = 2.1×10^3 s^{-1}. Subsequent theoretical studies by Somnitz and Zellner,[40] in which specific rate constants were evaluated via a RRKM treatment[41] with structural parameters and the energy barrier obtained from a modified G2 method,[40a] led to E_a = 17.33 kcal/mol, log(A) = 13.47 and k_∞(300 K) = 2.4 s^{-1}. The latter rate coefficient is close to the 1977 experimental value of 1.5 s^{-1} by Batt and Milne,[33e] and within about a factor of 2 of the 1999 experimental rate of 5.2 s^{-1} by Caralp et al.[35] Rauk et al.[30] used the composite CBS-RAD method and transition state theory (TST)[42] and obtained E_a = 16.8 kcal/mol, log(A) = 13.60 and k_∞ = 19 s^{-1} at 298 K. The C−C bond dissociation energies are 9.7 kcal/mol at 0 K and 11.4 kcal/mol at 298 K.[30] Recently, Neumark and co-workers[43] reported a photodissociation study of the ethoxy radical in the range 5−6 eV and analyzed their data using parts of the potential energy surface calculated at the B3LYP/6-311G++G** level.

Table 1 shows that after nearly five decades of work, no overall agreement or consistency has been reached yet on the formation enthalpies of the three $C_2H_5O^\bullet$ radicals. As pointed out above, a difference of 2−3 kcal/mol in the heats of formation can greatly influence the activation energies for hydrogen abstraction or decomposition, and quantitatively modify the rate constants and product branching ratios for ethanol combustion (by up to a factor of 10^2−10^3). In view of the uncertainty of the available results, we have reevaluated basic thermochemical parameters of $C_2H_5O^\bullet$ radicals by using current state-of-the-art electronic structure calculations. Extensive studies[44] have recently shown that an error bar of ±1.0 kcal/mol can be achieved for the calculated standard heats of formation of small organic compounds. When using a similar approach, we[45] have found that the heat of formation of acetaldehyde is 1.7 kcal/mol higher than the currently accepted value, namely $\Delta H^0_{f,298}(CH_3CHO) = -39.1 \pm 1$ kcal/mol (new theoretical value), instead of -40.8 ± 0.1 kcal/mol (current experimental value at 298.15 K), but closer to an earlier value of -39.7 ± 0.1 kcal/mol.[46] We also calculated the thermochemical values for methanol and its two radicals (CH_3OH, $CH_3O^\bullet$, and $C^\bullet H_2OH$) to further benchmark our method. In addition, the C−C bond energy of **3** and the transition state structure and rate coefficients for breaking the C−C bond were predicted.

Computational Methods

The calculations were performed by using the Gaussian 03[47] and MOLPRO[48] suites of programs. Geometry parameters of the structures were fully optimized and harmonic vibrational frequencies were calculated using molecular orbital theory at the second-order perturbation MP2 level with the correlation-consistent aug-cc-pVTZ basis set. The fully unrestricted formalism (UHF, UMP2) was used for open-shell system calculations done with Gaussian 03. Single-point electronic energies were calculated using the restricted coupled-cluster R/UCCSD(T) formalism in conjunction with the correlation-consistent aug-cc-pV*n*Z (n = D, T, and Q) basis sets, using (U)MP2/aug-cc-pVTZ optimized geometries. For simplicity, the basis sets are denoted hereafter as aV*n*Z. The CCSD(T) energies were extrapolated to the complete basis set (CBS) limit energies using the following expression[49]

$$E(x) = A_{CBS} + B \exp[-(x - 1)] + C \exp[-(x - 1)^2] \qquad (2)$$

Although, one can extrapolate the HF and correlation energies separately, on the basis of our experience, we have found that this does not substantially improve the fits.

After the valence electronic energy, the largest contribution to the total dissociation energy is the zero-point energy (ZPE). For methanol the fundamental vibrational frequencies are known from experiment.[50,51] Some of the fundamental vibrational frequencies for the radicals CH_3O and CH_2OH are also known.[52] Following the recommendations of Grev et al.,[53] we calculate the ZPE as the average of the calculated harmonic frequencies and the experimental fundamentals. For CH_3OH, this procedure yielded a scaling factor of 0.977, which was applied to the ZPE(MP2/aVTZ) values of the radicals and ions derived from CH_3OH. The same procedure was used for C_2H_5OH on the basis of the experimental values[54] for all modes except for the lowest two torsional modes which were taken from the calculations. This led to a scaling factor of 0.980, which was applied to the radicals and ions derived from C_2H_5OH. As discussed below, this procedure did not work for the radical cations derived from ionization of methanol and ethanol as the geometries and the harmonic frequencies had to be computed using the CCSD(T)/aVDZ method. We used scale factors for the radical cations of 0.985 and 0.988 taken as average of the calculated CCSD(T)/aVDZ harmonic frequencies and the experimental fundamentals for CH_3OH and C_2H_5OH respectively. There are two states for **3**, $^2A'$ and $^2A''$. $^2A''$ is lower in energy but has one imaginary frequency whereas the $^2A'$ state has all real frequencies. To evaluate the ZPE for **3**($^2A''$), we carefully matched the frequencies for the ^2A state derived from reducing the symmetry of $^2A''$ and replaced the imaginary frequency in the $^2A''$ state with the value of 565.5 cm^{-1} from the ^2A state. To calculate the kinetic parameters for the β-C−C bond scission, the geometry of **3**, in both $^2A'$ and $^2A''$ electronic states, and the transition structure (**3-TS**) were optimized at the MP2 and CCSD(T) levels with both the aVDZ and aVTZ basis sets. In addition, the frequencies were calculated at the MP2/aVTZ and CCSD(T)/aVDZ levels. We used the CCSD(T) frequencies with that for the $^2A''$ state corrected as described above.

To evaluate the total atomization energies, smaller corrections were also included. Core−valence corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[55] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass−velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[56] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. The spin−orbit corrections are 0.085 kcal/mol for C and 0.223 kcal/mol for O, both from the excitation energies of Moore.[57] For the ethoxy radical and its transition structure, we also calculated the molecular spin−orbit (SO) term that arises from the coupling between unpaired electron(s) in different lower-lying electronic states. The lowest spin−orbit coupled eigenstates were obtained by diagonalizing relatively small spin−orbit matrices in a basis of pure spin (Λ−S) eigenstates. In each case, the electronic states used as an expansion basis were restricted to two $^2A'$ and two $^2A''$ electronic states. The electronic states and SO matrix elements were obtained in singles-only multireference configuration interaction (MRCI) calculations with a full valence complete active space (CAS) reference function with the aug-cc-pVTZ-PP basis set using MOLPRO. Corrections due to the Born−Oppenheimer approximation have also been evaluated by calculating the diagonal correction (BODC),[58] at the HF/cc-pVDZ level, using the PSI3 program.[59]

For the purposes of comparison, the composite method G3[60] and its variation G3B3 have also been used. By combining our computed ΣD_0 values with the known heats of formation at 0 K for the elements ($\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal mol^{-1}, $\Delta H_f^0(O) = 58.99 \pm 0.1$ kcal mol^{-1}, and $\Delta H_f^0(H) = 51.63 \pm 0.001$ kcal mol^{-1}), we have derived ΔH_f^0 values at 0 K for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[61]

Results and Discussion

Total energies of the molecules are given in Table S1, calculated harmonic vibrational frequencies in Tables S2 and

TABLE 3: CCSD(T)/CBS Heats of Formation at 0 and 298 K (kcal/mol) Compared to Experiment

molecule	ΔH_f(0 K) this work	ΔH_f(0 K) expt	ΔH_f(298 K) this work	ΔH_f(298 K) expt
CH_3OH ($^{1}A'$)	−45.7	-45.44 ± 0.14^{a}	−48.3	$-48.04 \pm 0.14^{a,b}$
CH_3OH^+ ($^{2}A''$)	205.6		202.7	
CH_2OH (^{2}A)	−2.3	-2.75 ± 0.31^{c} -2.56 ± 0.17^{d}	−3.8	-3.97 ± 0.31^{e} -4.25 ± 0.31^{c} $-4.06 \pm 0.17^{d,f}$
CH_2OH^+ ($^{1}A'$)	171.2^{g}	171.6 ± 0.43^{c}	169.3^{g}	171.22 ± 0.31^{c}
CH_3O ($^{2}A'$)	7.4	6.79 ± 0.5^{d} 6.8 ± 0.4^{h}	5.5	$4.1 \pm 0.9^{a,b}$ $4.3 \pm 0.7^{i,j}$ 5.02 ± 0.5^{d} 5.11 ± 0.96^{k} 5.57 ± 0.22^{l}
H_3CO^- ($^{1}A_1$)	−29.1		−31.0	
H_3CO^+ ($^{3}A_1$)	253.9		252.1	
CH_3CH_2OH ($^{1}A'$)	−52.1	-51.96 ± 0.12^{a}	−56.4	$-56.12 \pm 0.12^{a,b}$
$CH_3C^{\bullet}HOH$ (**1**, ^{2}A)	−9.8	-10.5 ± 2^{m}	−13.1	$-15.2 \pm 1^{b,n}$ -13.7 ± 2^{m}
$C^{\bullet}H_2CH_2OH$ (**2**, ^{2}A)	−3.1	-5.5 ± 2^{m}	−6.2	$-7.5 \pm 1.7^{b,o}$ -8.7 ± 2^{m}
$CH_3CH_2O^{\bullet}$ (**3,** $^{2}A'$)	1.9		−1.7	
$CH_3CH_2O^{\bullet}$ (**3,** $^{2}A''$)	0.8	-0.05 ± 0.96^{d}	−2.7	$-3.6 \pm 0.8^{b,j}$ -3.25 ± 0.96^{d}
$CH_3CH_2O^{\bullet}$ (**3-TS,** $^{2}A'$)	18.0		14.7	
$CH_3CH_2OH^+$ ($^{2}A''$)	190.8		186.7	
CH_3CHOH^+ ($^{1}A'$)	145.7^{g}		142.2^{g}	
$CH_2CH_2OH^-$ (^{1}A)	−18.2		−21.4	
$CH_3CH_2O^-$ ($^{1}A'$)	−38.5		−42.1	

[a] Reference 66. [b] Referencd 5c. [c] Reference 6. [d] Reference 22. [e] Reference 74. [f] Reference 75. The value in this reference is not an experimental result; however, it matches that from ref 22. [g] Theoretical values taken from ref 45. [h] Reference 76. [i] Reference 77b. [j] Reference 29. [k] Reference 77a. This value was calculated at 300 K. [l] Reference 62. This is not an experimental result. [m] Reference 15. [n] Reference 9. [o] Reference 21.

TABLE 4: Calculated Thermochemical Parameters of Methanol and Its Radicals Compared to Experiment

method	ΔE_{rad},[b] kcal/mol	$IE_a(CH_3OH)$,[c] eV	$AE(CH_2OH^+)$,[g] eV	$IE_a(C^{\bullet}H_2OH)$,[c] eV	$EA(CH_3O^{\bullet})$,[j] eV	$IE_a(CH_3O^{\bullet})$,[c] eV	$\Delta H_{acid}(CH_3O{-}H)$,[m] kcal/mol	$PA(CH_3O^{\bullet})$,[q] kcal/mol
CBS[a]	9.7	10.90	11.64	7.52	1.58	10.69	381.8	167.5
G3	9.0	10.92^{d}	11.65	7.53	1.55	10.74	382.4	168.2
G3B3	8.7	10.90	11.65	7.54	1.53	10.70	382.5	
expt		10.90 ± 0.12^{e} 10.85 ± 0.03^{f}	11.65 ± 0.019^{h}	7.55 ± 0.01^{i}	1.572 ± 0.004^{k} 1.569 ± 0.0019^{l}	10.726 ± 0.008^{h}	381.7 ± 0.8^{n} 381.4 ± 0.7^{o} 380.7 ± 0.6^{p}	

[a] From the calculated heats of formation at 0 K unless noted in Table 3. [b] Relative energy between $^{\bullet}CH_2OH$ and $^{\bullet}CH_3O$, kcal/mol; see text. [c] Adiabatic ionization energy at 0 K. [d] The G3 result was obtained with an eclipsed conformation of the ionized methanol. [e] Reference 70. [f] Reference 71. [g] Appearance energy of CH_2OH^+ calculated from reaction 4. [h] Reference 72. [i] Reference 65. [j] Adiabatic electron affinity at 0 K. [k] Reference 77a. A similar value can be found in ref 13 (1.57 ± 0.022 eV). [l] Reference 81. [m] Gas phase acidity of methanol at 0 K. The calculated value at 298 K is 383.0 kcal/mol versus the experimental value 381.9 ± 0.6 kcal/mol.[29] [n] Reference 16. [o] Reference 76. [p] Reference 29. [q] Proton affinity at 298 K.

S3, and ZPEs and thermal corrections in Table S4 of the Supporting Information. MP2/aVTZ and CCSD(T)/aVDZ optimized geometries of the ethanol species are given in Table S5. The calculated total energies for **3** and **3-TS** at different geometries are given in Table S6. The components that are used to predict the total atomization energies (ΣD_0) and the ΣD_0 are given in Table 2. The predicted enthalpies of formation at 0 and 298 K are summarized in Table 3.

Methanol and Associated Radicals and Ions. The purpose of the present evaluation of the methanol energetics is a necessary calibration for our study of ethanol. For a reasonably complete list of previous studies on the $C^{\bullet}H_2OH$ and $CH_3O^{\bullet}$ radicals derived from methanol, refer to the earlier work of Johnson and Hudgens,[6] and the more recent IUPAC compilation by Ruscic et al.[22] Table 4 summarizes thermochemical parameters of methanol and $CH_3O^{\bullet}$ radicals. For comparison, the G3 and G3B3 results are also tabulated in Table 4.

The $C^{\bullet}H_2OH$ radical is nonplanar as expected due to the electronegative character of the OH group. With respect to the planar structure of the parent methyl radical, the hydroxy group induces a small out-of-plan distortion and a slightly pyramidal carbon center. The coupling between the OH internal rotation and the CH_2 wagging mode, and its effects on thermochemical parameters of the radical have been analyzed in detail in previous studies.[6,22] The corresponding cation CH_2OH^+, which is the protonated form of formaldehyde, is planar. Under the C_{3v} point group, the SOMO of $CH_3O^{\bullet}$ is doubly degenerate, and as a consequence, its geometry is subject to a Jahn−Teller (JT) distortion, which lowers its symmetry. The stabilizing distortion to the C_s point group reduces one HCO bond angle from 109.7° to 104.9° but enlarges the two other HCO angles to 112.5°, giving a $^{2}A'$ C_s energy minimum. The $^{2}A''$ state is an energy maximum with a negative frequency. The open-shell nature of the electronic system allows spin−orbit interactions, which further split the degeneracy of the vibronic states, which in turn modifies the vibrational levels and the zero-point energies. The interplay between both effects was recently investigated using high-quality wavefunctions by Marenich and Boggs.[62] The JT stabilization energy (the difference between both ^{2}E and $^{2}A'$ states) is 0.77 kcal/mol (270 cm^{-1}), whereas the barrier to pseudorotation (the difference between both $^{2}A''$ and $^{2}A'$ states) is only 0.14 kcal/mol (49 cm^{-1}). Although the energy difference is very small, the $^2A'$ state formally corresponds to the electronic ground state of the methoxy radical. We note that the present results for the geometrical parameters, vibrational frequencies, and thermal corrections of both (CH_3O) radicals compare well with those selected in the IUPAC list.[22]

The methoxide anion CH_3O^- possesses a C_{3v} singlet state ($^1A_1$), whereas the CH_3O^+ cation exhibits a C_{3v} structure with a triplet ground state ($^3A_1$). Both ions are stable with respect to JT distortions. In general, geometrical parameters predicted by using the (U)MP2/aVTZ method compare well with experimental data. The MP2-bond distance of 1.423 Å of C−O in methanol is close to the well-established microwave result of 1.428 Å.[63] This distance is shortened in both radicals, to 1.366 Å in $C^{\bullet}H_2OH$ and 1.377 Å in $CH_3O^{\bullet}$ (exptl: 1.37 ± 0.02 Å).[64]

The CCSD(T)/CBS calculated values $\Delta H^0_f(CH_3OH) = -45.7$ and -48.3 kcal/mol at 0 and 298 K, respectively (Table 3), are in good agreement with the experimental values -45.44 ± 0.14 and -48.04 ± 0.14 kcal/mol.[65,66] A slightly more negative experimental value of -49.0 ± 1.0, $\Delta H^0_f(CH_3OH)$ at 298 K, was tabulated in the recent Sandia database,[67] but this value seems to be somewhat too low. The most recent NASA compilation[5] adopts the value -48.04 ± 0.14 kcal/mol for 298 K.

The geometry of the radical cation generated by removing and ionizing CH_3OH is strongly dependent on the theoretical method employed.[68] Geometry optimizations at either the UMP2 or UB3LYP level, with the aVDZ and aVTZ basis sets, agree with earlier findings that ionized methanol has an eclipsed conformation (HCOH dihedral angle equal to zero). The two H-atoms are situated in a cis-configuration with respect to the C−O bond, within the C_s molecular plane, in contrast with neutral methanol with a staggered *trans*-HCOH conformation. The energy difference between the eclipsed (cis) and staggered (trans) conformers in the cation based on fully optimized geometries without ZPE corrections is 0.42 kcal/mol at the UCCSD(T)/aVTZ level and is essentially doubled to 0.88 kcal/mol at the UB3LYP/aVTZ level. A similar change in conformation of the methyl group following ionization was also noted in methyl formate.[69] The calculated C−O bond distance of ionized methanol is method dependent. It is expected to decrease relative to CH_3OH, due to removal of an electron from the antisymmetric 2a″ HOMO of methanol. The C−O distance in the ground state of the methanol radical cation ($^2A''$) is calculated as 1.38 Å at the UB3LYP/aVTZ level, 1.39 Å at the UCCSDT/aVDZ level, but only 1.30 Å at the UMP2/aVTZ level. Compared to the CCSD(T) C−O distance, the UMP2 distance is too short. We optimized the geometry of CH_3OH^+ at the CCSD(T)/aVDZ level and calculated its ZPE at the same level. The calculated value, $\Delta H^0_f(CH_3OH^{\bullet +}) = 205.6$ kcal/mol at 0 K, leads to an adiabatic ionization energy of $IE_a(CH_3OH) = 10.90$ eV, in excellent agreement with an early experimental value of 10.90 ± 0.12 eV.[70] Our calculated value is also in good agreement with the most recent experimental value, 10.85 ± 0.03 eV.[71] If the MP2 geometry is used, $IE_a(CH_3OH) = 11.05$ eV, an error of 0.15 eV or 3.4 kcal/mol. The G2 method, which is based on UMP2 geometries, overestimates $IE_a(CH_3OH)$ by 0.06 eV, giving 10.96 eV.[68] The G3 method ($IE_a(CH_3OH) = 10.92$ eV) and the G3B3 method, which is based on B3LYP/6-31G(d) geometries ($IE_a(CH_3OH) = 10.89$ eV), yield ionization energies in good agreement with our value.

Our predicted value for $\Delta H^0_{f,0}(C^{\bullet}H_2OH)$ is -2.3 kcal/mol. Recent experimental values have been reported for this quantity: $\leq -2.1 \pm 0.7$ kcal/mol[72] and -2.75 ± 0.31 kcal/mol.[5,6,73] Our value is in good agreement with either value considering the experimental error limits. Our calculated value for $\Delta H^0_{f,298}(C^{\bullet}H_2OH)$ of -3.8 kcal/mol is in agreement with the corresponding experimental results at 298 K of -3.97 ± 0.31 kcal/mol[74] and -4.25 ± 0.31 kcal/mol.[5,6] Our calculated value for $\Delta H^0_{f,298}(C^{\bullet}H_2OH)$ is also in agreement with the most recent theoretical value of -4.06 ± 0.17 kcal/mol, obtained by Marenich and Boggs[75] using a comparable computational approach. The value -4.06 ± 0.17 kcal/mol was selected in the recent IUPAC compilation[22] as the preferred heat of formation for the hydroxymethyl radical. The corresponding value at 0 K is -2.56 ± 0.17 kcal/mol.

Our work differs from the computational study by Marenich and Boggs[75] in two ways: (i) they used $CH_2OH \rightarrow CH_2O + H$ as the working equation for evaluating the heat of formation whereas we used the atomization reaction and (ii) they explicitly evaluated anharmonic frequencies to estimate the ZPEs whereas we used a simpler approach with scaling factors. Both theoretical approaches led to essentially the same heat of formation with a difference of less than 0.3 kcal/mol.

A value of $\Delta H^0_{f,0}(CH_3O^{\bullet}) = 7.4$ kcal/mol is predicted at 0 K, in good agreement with the value of 6.8 ± 0.4 kcal/mol reported by Neumark and co-workers.[76] The corresponding calculated value at 298 K is $\Delta H^0_{f,298}(CH_3O^{\bullet}) = 5.5$ kcal/mol, more positive than the value of 4.1 ± 0.9 kcal/mol in the NASA compilation, by 1.4 kcal/mol.[19] Marenich and Boggs[62] obtained $\Delta H^0_{f,298}(CH_3O^{\bullet}) = 5.57 \pm 0.22$ kcal/mol using the approach described above including the molecular spin−orbit corrections; this value is in excellent agreement with our result. A more recent value of 4.3 ± 0.7 kcal/mol,[29,77b] derived from an experimental bond dissociation enthalpy of $BDE_{298}(CH_3O{-}H) = 104.6 \pm 0.7$ kcal/mol is less positive than ours by 1.0 kcal/mol. Our predicted values are in agreement with the values of 6.79 ± 0.5 kcal/mol at 0 K and 5.02 ± 0.5 kcal/mol at 298 K, selected as the preferred enthalpies of formation for methoxy radical in the IUPAC compilation.[22]

The calculations confirm that $C^{\bullet}H_2OH$ is more stable than $CH_3O^{\bullet}$ (ΔE_{rad} in Table 4) by 9.7 kcal/mol at 0 K and by 9.3 kcal/mol at 298 K. The corresponding G3 and G3B3 values of 9.0 and 8.7 kcal/mol values as well as the previous G2 value[78] of 8.8 kcal/mol for ΔE_{rad} are in agreement with our value. ΔE_{rad} also corresponds to the difference between the C−H and O−H bond energies in methanol. This is significantly smaller than the separation of 14.2 kcal/mol between the BDEs of C−H bond in methane (103.4 kcal/mol) and O−H in water (117.6 kcal/mol).[29]

Previous quantum chemical results for $\Delta H^0_{f,0}(C^{\bullet}H_2OH)$ range from -2.1 to -2.9 kcal/mol.[6,78,75] In most previous theoretical studies, evaluation of the heat of formation was done using isodesmic reactions such as reaction 3.[6] Using the experimental[65]

$$C^{\bullet}H_2OH + CH_4 \rightarrow CH_3OH + C^{\bullet}H_3 \qquad (3)$$

heats of formation at 0 K of CH_4 (-15.99 ± 0.10 kcal/mol), CH_3OH (-45.44 ± 0.14 kcal/mol), and $C^{\bullet}H_3$ (35.62 ± 0.07 kcal/mol) and the calculated value for the reaction energy at the CBS limit of 8.6 kcal/mol, we obtain $\Delta H_f(C^{\bullet}H_2OH) = -2.4$ kcal/mol at 0 K, the same as obtained from the atomization energies (-2.3 kcal/mol). A value of 8.5 kcal/mol for this reaction energy was reported on the basis of UCCSD(T)/CBS calculations.[79] Compared with our CCSD(T)/CBS result, the heat of formation of CH_2OH is underestimated by 1.3 kcal/mol at the G3/G3B3 level.

Johnson and Hudgens[6] employed the CBS-QCI/APNO method for calculating the enthalpy of reaction 3 and obtained $\Delta E_r(3) = 9.1$ kcal/mol at 0 K. This differs by 0.6 kcal/mol from our

TABLE 5: Thermochemical Parameters of Ethanol and Its Radicals Compared to Experiment

method	ΔE(**2**−**1**),[b] kcal/mol	ΔE(**3**−**1**),[c] kcal/mol	AE(CH_3CHOH^+),[d] eV	IE_a(C_2H_5OH),[f] eV	IE_a(**1**),[f] eV	EA(**3**, $^2A''$),[i] eV	ΔH_{acid}(C_2H_5OH),[l] kcal/mol	PA(**3**),[o] kcal/mol
CBS[a]	6.7	10.6	10.82	10.53	6.74	1.70	378.8	176.3
G3	7.5	10.1	10.81		6.75	1.71	378.5	
G3B3	6.9	9.6	10.87		6.76	1.73	378.5	
expt			10.801 ± 0.005[e]	10.48 ± 0.07[g]	6.78	1.712 ± 0.004[j]	378.6 ± 0.8[m]	
					6.64 ± 0.03[h]	1.726 ± 0.033[k]	377.6 ± 0.7[n]	

[a] From the calculated heats of formation at 0 K unless noted in Table 3. [b] Relative energy between $C^\bullet H_2CH_2OH$, **2**, and $CH_3C^\bullet HOH$, **1**. [c] Relative energy between $CH_3CH_2O^\bullet$ (**3**, $^2A''$), and $CH_3C^\bullet HOH$, **1**. [d] Appearance energy from eq 6. [e] Reference 15. [f] Adiabatic ionization energy. [g] Reference 65. [h] Reference 17. [i] Adiabatic electron affinity. [j] Reference 77a. [k] Reference 13. [l] Gas phase acidity of ethanol at 0 K. The calculated value at 298 K is 380.0 kcal/mol versus the experimental value of 378.7 ± 0.8 kcal/mol.[29] [m] Reference 16. [n] Reference 29. [o] Proton affinity of the radical **3** ($^2A''$) at 298 K.

present result (8.5 kcal/mol). The difference is due in part to their use of experimental fundamental vibrational frequencies for evaluating the ZPEs.[6] We used the average of the experimental and best (available) theoretical ZPEs as an estimate for this correction. The two approaches differ by about 0.4 kcal/mol for the effect of the ZPE on $\Delta E_r(3)$.

The loss of H gives the CH_2OH^+ ion whose appearance energy was experimentally[68] determined as the energy of reaction 4. Our calculated value of 11.64 eV for this reaction is

$$CH_3OH \rightarrow CH_2OH^+ + H + e^- \qquad (4)$$

in very good agreement with the experimental result, 11.65 ± 0.019 eV.[72] The calculated ionization energy of the hydroxymethyl radical is 7.52 eV, in good agreement with the experimental value of 7.55 ± 0.01.[72] The calculated value for $\Delta H_{f,298}(CH_2OH^+) = 169.3$ kcal/mol is the same as that derived from the experimental proton affinity of formaldehyde, PA(CH_2O) = 170.4 kcal/mol at 298 K.[6,11] Our calculated value for PA(CH_2O) is 170.4 kcal/mol at 298 K.[45]

Two distinct experimental results of 7.37 ± 0.03[80] and 10.726 ± 0.008 eV[72] have been reported for the ionization potential of $CH_3O^\bullet$. Our calculated value for $IE_a(CH_3O^\bullet)$ of 10.69 eV differs from the higher value by only 0.04 eV, less than 1 kcal/mol, and clearly the lower value is incorrect. The calculated electron affinity (EA) for $CH_3O^\bullet$ of 1.58 eV is in good agreement with the experimental results of 1.570 ± 0.022,[13] 1.572 ± 0.004,[77a] and 1.5690 ± 0.0019 eV.[81] The methoxide anion CH_3O^- is far more stable than its CH_2OH^- isomer, which is unstable with respect to electron detachment. As expected, the acidity of methanol is due to O-deprotonation. The calculated gas phase acidity $\Delta H_{acidity}(CH_3O-H) = 381.8$ kcal/mol is in agreement with the spectroscopic determinations of 381.4 ± 0.7[76] and 381.7 ± 0.8 kcal/mol.[16] By using the calculated (CBS) heat of formation of formaldehyde, $\Delta H_f(CH_2O) = -25.1$ kcal/mol at 0 K,[45] and the CBS result for $CH_3O^\bullet$ (Table 3), we find the C−H bond strength in the radical to be 19.1 kcal/mol, only 0.7 kcal/mol less than the experimental estimate of 19.8 ± 0.4 kcal/mol.[76] The proton affinity of methoxy radical can be calculated from our data, PA($CH_3O^\bullet$) = 167.5 kcal/mol (at 298 K).

Overall, our calculated results for the thermochemical parameters of the methanol derivatives agree quite well with available experimental data, with deviations amounting to, at most, ± 0.5 kcal/mol. On the basis of these results and our estimates of the errors in the ZPEs for the molecules derived from ethanol, we estimate the errors for the molecules derived from C_2H_5OH discussed below to be ± 0.8 kcal/mol.

Ethanol and Associated Radicals and Ions. Table 4 lists the heats of formation at 0 and 298 K of ethanol and three ($C_2H_5O^\bullet$) radicals, whereas Table 5 summarizes additional thermochemical data. The calculated CCSD(T)/CBS values for $\Delta H_f(C_2H_5OH)$ of −52.1 kcal/mol at 0 K and −56.4 kcal/mol at 298 K are in good agreement with the experimental values of −51.96 ± 0.12 and −56.12 ± 0.12 kcal/mol, respectively.[5,66]

The 1-hydroxyethyl radical (**1**) has a nonplanar carbon radical center (C_1). The presence of a methyl and a hydroxyl group leads to two distinct equilibrium conformers. Curtiss et al.[25] found the anti CCOH conformer to be more stable than the OH gauche conformer by 0.3 kcal/mol at the G2 level. Our UMP2/aVTZ calculations concur with this finding, which show an energy difference of 0.4 kcal/mol (with ZPE) in favor of the anti form. The fully planar conformer (C_s, $^2A''$) is characterized by a negative frequency ($\nu_i = 513i$ cm^{-1}) and corresponds to the transition structure for inversion at the carbon center. The energy difference between both planar and pyramidal anti forms of **1** is small, 1.0 kcal/mol without ZPE, but only 0.2 kcal/mol when ZPE corrections are included. For our final energies, we used the lowest energy anti conformer for **1**.

The 2-hydroxyethyl radical **2** possesses several possible conformers. In agreement with conformational analyses carried out in previous studies,[24,25,26] the anti and gauche forms of the CCOH moiety constitute the two energetically lowest-lying conformers of **2**. The anti form with a dihedral angle ∠CCOH of 174.7° (UMP2/aVTZ) is less stable than the gauche form with ∠CCOH = 54.7°. At the UCCSD(T)/CBS limit, the gauche form is 0.83 kcal/mol lower in energy than the anti. The gauche structure has a larger ZPE than the latter by 0.31 kcal/mol. Thus, the gauche conformer of **2** is 0.52 kcal/mol than the anti including ZPE corrections. The planar C_s structures of **2** possess one, or even two, negative vibrational frequencies and are therefore transition structures for either carbon inversion or CH_2 and OH group rotations. The barrier to inversion at the terminal radical center of the anti form is less than 0.1 kcal/mol, showing an essentially planar geometry at the C radical center. For our final energies, we used the lowest energy the gauche conformer for **2.** The UMP2/aVTZ optimized geometries of the low-lying conformers of **1** and **2** are given in Supporting Information (Table S5).

The equilibrium structure of ethoxy radical **3** has a staggered configuration. The eclipsed configuration corresponds to a transition structure for rotation of the methyl group. Radical **3** has two low-energy electronic states. The methoxy homologue $CH_3O^\bullet$ is subject to a Jahn−Teller distortion that lowers its symmetry from C_{3v} to C_s and splits the ^2E electronic state to $^2A'$ and $^2A''$, with $^2A'$ being the ground state. Replacing one H atom of $CH_3O^\bullet$ by a methyl group gives $CH_3CH_2O^\bullet$ and lifts the formal degeneracy of the e molecular orbital centered at the oxygen atom in $CH_3O^\bullet$, generating $^2A'$ and $^2A''$ electronic states for **3**. In their earlier paper, Sosa and Schlegel[24] stated, “Like CH_3O, the ethoxy radical has [an] A′ ground state”. Curtiss et al.[25] later reported: “The ground state of [the] ethoxy radical is $^2A''$. The $^2A'$ state is only 0.7 kcal/mol less stable at

TABLE 6: Optimized Geometries of the Ethoxy Radical 3 in Different Electronic States and of the Transition Structure 3-TS[a]

method	r_{C1-C2}	r_{C2-O3}	r_{C1-H4}	r_{C1-H5}, r_{C1-H6}	r_{C2-H7}, r_{C2-H8}	$\angle_{O3-C2-C1}$	$\angle_{H4-C1-C2}$	$\angle_{H5-C1-C2}$	$\angle_{H7-C2-C1}$	$\angle_{H5-C1-C2-H4}$[b]	$\angle_{H7-C2-C1-O3}$[b]
					Ethoxy Radical **3** ($^2A'$)						
MP2/aVDZ	1.542	1.393	1.100	1.099	1.105	106.0.	108.6	110.5	109.4	119.5	119.6
MP2/aVTZ	1.533	1.382	1.088	1.087	1.094	105.8	108.7	110.4	109.4	119.6	119.6
CCSD(T)/aVDZ	1.554	1.394	1.104	1.103	1.110	106.0	108.3	110.3	109.7	119.6	119.7
CCSD(T)/aVTZ	1.544	1.381	1.092	1.090	1.098	105.8	108.4	110.2	109.0	119.6	119.8
					Ethoxy Radical **3** ($^2A''$)						
MP2/aVDZ	1.526	1.392	1.102	1.100	1.110	114.7	110.4	110.4	111.9	120.0	121.3
MP2/aVTZ	1.517	1.380	1.090	1.088	1.098	114.6	110.5	110.3	111.8	120.1	121.4
CCSD(T)/aVDZ	1.533	1.393	1.106	1.104	1.116	114.9	110.4	110.3	111.9	120.1	121.6
CCSD(T)/aVTZ	1.522	1.380	1.094	1.092	1.104	114.8	110.6	110.2	111.9	120.2	121.6
					Ethoxy Radical **3** (^2A)[c]						
MP2/aVDZ	1.527	1.391	1.101	1.099/ 1.099	1.111/ 1.107	114.4	110.3	110.4/ 110.3	111.1/ 112.2	120.4/ −119.6	117.0/ −125.1
MP2/aVTZ	1.518	1.379	1.090	1.088/ 1.088	1.101/ 1.096	114.4	110.4	110.4/ 110.3	111.1/ 112.2	120.4/ −119.7	117.0/ −125.4
CCSD(T)/aVDZ	1.534	1.393	1.106	1.104/ 1.104	1.118/ 1.113	114.6	110.3	110.4/ 110.2	111.0/ 112.4	120.4/ −119.6	117.6/ −125.3
					Transition Structure **3-TS** ($^2A'$)						
MP2/aVDZ	2.054	1.213	1.081	1.078	1.104	103.6	99.9	99.5	90.6	120.3	122.9
MP2/aVTZ	2.065	1.224	1.093	1.091	1.115	103.5	99.7	99.9	90.7	120.2	122.9
CCSD(T)/aVDZ	2.151	1.251	1.098	1.096	1.114	103.2	99.3	99.7	91.0	120.1	122.1
CCSD(T)/aVTZ	2.152	1.238	1.084	1.082	1.102	103.3	99.4	99.2	90.6	120.2	122.1

[a] Bond distances (*r*) in angstroms (Å) and bond angles (∠) in degrees (°). The atom numbering is defined in Figure 1. The structure has C_s point group for **3**($^2A'$), **3**($^2A''$) and **3-TS** with a H4−C1−C2−O3 dihedral angle equal to 180°. Geometrical parameters of CH_2O and CH_3 are given in Table S5. [b] These values are ± depending on which of the two equivalent angles by symmetry is chosen. [c] This corresponds to a distortion from the $^2A''$ state structure. The H4−C1−C2−O3 dihedral angle is equal to 182.0° (MP2/aVDZ), 182.1° (MP2/aVTZ) and 181.9° (CCSD(T)/aVDZ). Each C_s parameter of CH_2 groups is split into two different values for CH distances and CCH bond angles, and the + (H_5 and H_7) and − (H_6 and H_8) dihedral angles.

the G2 level and is also staggered". In the recent IUPAC compendia,[22] the $^2A''$ state was assigned as the ground state of **3**.

Our optimized geometries at various levels are summarized in Table 6. The $^2A'$ state is found to be an energy minimum, with all positive vibrational frequencies, at all levels of theory considered: B3LYP, HF, MP2 and CCSD(T). This state is characterized by a ∠CCO bond angle of ~106°, which is smaller than the angle in CH_3CH_2OH. The C−C and C−O bond distances are 1.54−1.55 and 1.38−1.39 Å, respectively.

The $^2A''$ state is lower in energy than the $^2A'$ state for **3**. At the HF or MP2 methods, irrespective of the basis set up to aVTZ, a single imaginary frequency corresponding to torsion of the central CH_2 group is predicted. At the B3LYP level, an imaginary frequency is found with small basis sets, but the $^2A''$ structure becomes a real minimum with more extended basis sets, beginning with basis sets of 6-311G(d,p) quality. At the UCCSD(T)/aVDZ level, the $^2A''$ structure is a saddle point with one imaginary frequency. The imaginary frequency is calculated to be 425i cm^{-1} at the MP2/aVTZ level and 358i cm^{-1} at CCSD(T)/aVDZ. Relative to the $^2A'$, this state is characterized by a larger ∠CCO = 114−115° bond angle and a slightly shorter C−C distance (1.52−1.53 Å). The C−O bond distance of 1.38−1.39 Å remains unchanged. Relaxation of the $^2A''$ geometry following the imaginary mode leads to a distorted structure with a small twisting of the central methylene group by 3−4°. Apart from this distortion, the C−C and C−O distances, the ∠CCO bond angle, and the methyl moiety remain essentially the same as those in the $^2A''$ state (Table 6). The energy gain upon geometry relaxation from $^2A''$ C_s to ^2A C_1 is extremely small, 0.03 kcal/mol at the UMP2/aVTZ level. The small energy difference, which is below the zero-point energy of the lowest mode (0.35 kcal/mol), and the fact that we are in the harmonic approximation lead us to conclude that the $^2A''$ (C_s) state will be the structure observed under any conditions.

In contrast to $CH_3O^•$, the $^2A'$ state in **3** is higher in energy than the $^2A''$ state. Our best estimates at the UCCSD(T)/CBS level result in an energy gap $\Delta E(^2A'-^2A'')$ of 0.48 kcal/mol at the valence electronic energy level and 1.1 kcal/mol (0 K with all corrections incorporated) in favor of the $^2A''$ state. At 298 K, this gap is slightly reduced to 1.0 kcal/mol (Table 3). In a recent photoelectron study of the ethoxy anion, Ramond et al.[77a] assigned the first peak in the PES spectrum as the EA(**3**) = 1.67 eV and identified a nearby peak as originating from a lower-lying excited state of the neutral. The A−X energy gap of **3** was accordingly determined as $T_0 = 355 \pm 10$ cm^{-1} (0.044 eV or 1.01 kcal/mol). Our value is in excellent agreement with the experimental T_0. The G3B3 value of 0.97 kcal/mol for this $^2A'-^2A''$ separation[22] is in agreement with our higher level value. Foster et al.[82] analyzed the rotationally resolved spectrum of jet-cooled ethoxy radical and showed that the rotational signature is due to a $^2A''$ ground state, again consistent with our conclusion. In the following discussion, the electronic ground state for the ethoxy radical **3** is $^2A''$.

Due to the conformational flexibility of **3**, evaluation of the ZPEs for the two states is not straightforward. In the IUPAC compilation,[22] a ZPE of 39.6 kcal/mol was derived for the ground state of **3**, from vibrational frequencies for the distorted C_1 (^2A) structure obtained at the UB3LYP/6-31G(d) level scaled by a factor of 0.9614. The approach used to estimate the ZPE for the electronic states of $^2A''$ state of **3** is described above. Our best estimate is from CCSD(T)/aVDZ harmonic frequencies scaled by 0.988 and is 40.32 kcal/mol.

The eclipsed configuration lies higher in energy for both states of **3**. The energy differences between both eclipsed and staggered forms are 2.1 and 2.5 kcal/mol for the $^2A'$ and $^2A''$, respectively (UMP2/aVTZ). Thus, at the eclipsed conformation, the potential surfaces of both electronic states are essentially degenerate.

The potential lowering of the electronic energy due to the molecular spin−orbit interactions was also evaluated. The corrections are negligible for all of the structures **1** (−0.02

cm^{-1}), **2** (0.00 cm^{-1}), the state $^2A''$ of **3** (3.09 cm^{-1}), and **3-TS** (−0.08 cm^{-1}).

The most stable isomer among the radicals generated by loss of H from CH_3CH_2OH is **1**. At 0 K, it is 6.7 and 10.6 kcal/mol more stable than **2** and **3**, respectively. This is in agreement with the general experimental ordering. The calculated values for $\Delta H_f(\mathbf{1})$ are −9.8 kcal/mol at 0 K and −13.1 kcal/mol at 298 K. The 298 K value can be compared to the experimental values of −15.2 ± 1.0[5,9] and −13.7 ± 2 kcal/mol.[15] We recommend the latter value from a photoionization experiment[15] although our value would be consistent with the lower range of the value obtained from the kinetic experiment.[9] The calculated values for $\Delta H_f(\mathbf{2})$ are −3.1 kcal/mol at 0 K and −6.2 kcal/mol at 298 K. The 298 K value can be compared to the experimental values of −13.5 ± 3,[14] −8.7 ± 2,[15] −7.5 ± 1.7,[21] and −2.5 kcal/mol.[10] Our value is in good agreement with the photoionization experiment[15] and the tabulated results of Fulle et al.[21] Ruscic and Berkowitz[15] found an energy difference between **1** and **2** of 5.0 kcal/mol based on photoionization data as compared to our calculated energy difference of 6.7 kcal/mol. Our calculated values for $\Delta H_f(\mathbf{3})$ of +0.8 kcal/mol at 0 K and −2.7 kcal/mol at 298 K can be compared with those of +1.0 and −2.37 kcal/mol, obtained by Rauk et al.[30] using the CBS-RAD method. Inclusion of the A′ excited state in the calculation of $\Delta H_f(\mathbf{3})$ at 298 K would increase the heat of formation by 0.18−0.25 kcal/mol depending on whether the lowest energy torsion is treated as a vibration 9 (former) or as a hindered rotor (latter). The theoretical value at 298 K of −2.3 kcal/mol obtained using the ccCA method[32] is similar to our value. The 298 K value can be compared to the experimental values of −6 ± 2,[13] −3.7 ± 0.8,[16] and +4.1[10] kcal/mol. The IUPAC preferred values[22] for **3** are −0.05 ± 0.96 and −3.25 ± 0.96 kcal/mol at 0 and 298 K, respectively and our values are in excellent with these values as well as the experimental determination of −3.7 ± 0.8 kcal/mol[16] from gas phase acidities. Because the acidity and the radical electron affinity were measured with small uncertainty, the heat of formation of the radical can also be determined with higher accuracy.

The G2 enthalpy of formation of −9.7 kcal/mol (at 0 K)[25] for **1** is in excellent agreement with the present result of −9.8 kcal/mol. The agreement between the G2 value of −2.7 kcal/mol for $\Delta H_f(\mathbf{2})$ and the present value of −3.1 kcal/mol is only slightly worse (0.4 kcal/mol), and the largest difference (0.7 kcal/mol) is for $\Delta H_f(\mathbf{3})$ with a G2 value of 0.1 kcal/mol as compared to our value of 0.8 kcal/mol at 0 K. Relative to the CCSD(T)/CBS values, the G3 and G3B3 results are within their expected accuracy, with differences of about 1.0 kcal/mol. Overall, the composite methods perform well, except for the cases where the geometries are not well reproduced by the MP2 or B3LYP methods.

We can examine the consistency of our predicted values with respect to currently available thermochemical data by using a working reaction similar to (3) for the β-hydroxy isomer **2**. Reaction 5 was previously used[26a] to evaluate the formation enthalpy of the radical, and its H-abstraction mechanism was also investigated in detail.[31] Taking the experimental value

$$C^\bullet H_2CH_2OH + CH_4 \rightarrow CH_3CH_2OH + C^\bullet H_3 \qquad (5)$$

$\Delta H_{f,0}(C_2H_5OH) = -51.96$ kcal/mol, and those of CH_3 and CH_4 quoted above, the radical $\Delta H_{f,0}$ can be derived from the calculated energy of the reaction 5, of 2.8 kcal/mol. We calculate $\Delta H_f(\mathbf{2}) = -3.1$ kcal/mol at 0 K the same as from the atomization energy approach.

As in methanol, ionized ethanol has, in its $^2A''$ ground state, an eclipsed CCOH configuration. The staggered conformation of ionized ethanol exhibits one imaginary frequency and is a transition structure for methyl rotation. The energy difference between both staggered and eclipsed configurations amounts to 1.37 kcal/mol (without ZPE) and 0.84 kcal/mol (with ZPE) at the CCSD(T)/aVTZ level. The C−O bond distance is shortened on removal of an electron. Again, the UMP2 method markedly overestimates the shortening of this bond to 1.31 Å, as compared with those of 1.36 Å by UB3LYP and 1.38 Å by UCCSD(T). Following our work on CH_3OH, we used the UCCSD(T)/aVDZ optimized geometry for evaluating the CCSD(T)/CBS energy and ZPE correction. The calculated ionization energy of ethanol, $IE_a(C_2H_5OH) = 10.53$ eV, is within the error limits of the experimental value of 10.48 ± 0.07 eV.[65] Replacement of methyl by ethyl leads to a reduction of 0.37 eV for the alcohol IE_a. If the MP2 geometry is used for the cation, $IE_a(CH_3CH_2OH) = 10.76$ eV, a substantial error of 0.23 eV (5.4 kcal/mol).

Following ionization of ethanol, loss of H gives the CH_3CHOH^+ ion whose appearance energy was experimentally[15] determined as the energy of reaction 6. Our calculated appearance energy $AE(CH_3CHOH^+)$ agrees to within 0.02 eV with the experimental value of 10.801 ± 0.005 eV. We recently determined the proton affinity of acetaldehyde as 184.4 kcal/mol and $\Delta H_f(CH_3CHOH^+) = 145.7$ kcal/mol at 0 K and 142.2 kcal/mol at 298 K.[45] Our proton affinity value is in good agreement with the experimental value of Ruscic and Berkowitz,[15] ≥183.8 ± 0.2 kcal/mol, and the tabulated experimental value of 183.7 ± 0.4 kcal/mol.[83]

$$CH_3CH_2OH \rightarrow CH_3CHOH^+ + H + e^- \qquad (6)$$

A photoelectron measurement of the ionization energy of the C_α radical gives $IE_a \leq 6.85$ eV.[15] The uncertainty was due to the shallow onset of the photoion yield curve for the cation, which limited the accuracy of the measured IE. An adiabatic value, $IE_a(\mathbf{1}) = 6.78$ eV, was recommended by these authors.[15] The adiabatic and vertical IEs of **1** have also been measured using ultraviolet photoelectron spectroscopy as 6.64 ± 0.03 and 7.29 ± 0.03 eV, respectively.[17] With the UMP2/aVTZ optimized geometry of **1**, the calculated electronic energies of both neutral **1** and cation CH_3CHOH^+ provide the vertical IE of **1**. For this quantity, we obtain a value of 7.41 eV at the CCSD(T)/aVTZ level, 0.12 eV larger than the experimental measurement of Dyke et al.[17] Similarly, our calculated adiabatic ionization energy of $IE_a(\mathbf{1}) = 6.74$ eV, at 0 K (Table 5), is closer to the earlier value of Ruscic et al.,[15] 6.78 and 0.10 eV larger than the Dyke et al. result. The G3 and G3B3 methods also led to larger values 6.75 and 6.76 eV for $IE_a(\mathbf{1})$ at 0 K, respectively, in excellent agreement with our value. In comparison with the PES results of Dyke et al.,[17] we predict a relaxation energy of 0.67 eV in going from the vertical ion to its equilibrium position, essentially the same as the value of 0.65 eV obtained by Dyke et al.[17] There appears to be a systematic shift of ∼0.10 eV to lower values in the experimental PES analysis. The good agreement between theory and some of the experiments for the quantities $\Delta H_f(CH_3CHOH^+)$ and $IE_a(\mathbf{1})$ further supports our calculated values for $\Delta H_f(\mathbf{1}) = -9.8$ kcal/mol at 0 K and −13.1 kcal/mol at 298 K.

We predict that the electron affinity of the C_α radical **1** is 0.65 eV at 0 K. The structure has the O−H bond eclipsing the C−C bond to stabilize the carbanion center. If the hydrogen on the OH group does not stabilize the carbanion center, the anion is predicted to be unstable to loss of an electron with a negative electron affinity of −0.24 eV at the G3 level. We predict the

β-radical **2** to have a slightly larger electron affinity of 0.65 ± 0.04 eV. The ethoxy radical **3** has an even larger electron affinity at 0 K of 1.70 eV (1.71 eV at 298 K), which is in agreement with the experimental values 1.712 ± 0.004[77a] and 1.726 ± 0.033 eV.[13] Comparing these to a value of EA($CH_3O^•$) = 1.54 eV indicates that the larger alkyl group exerts a further stabilization of the alkoxide anion. In addition, the ethoxide anion is about 20 kcal/mol more stable than its C_β-ethyl anion isomer.

We predict the following set of bond dissociation enthalpies at 0 K: BDE($CH_3CHOH-H$) = 93.9 kcal/mol, BDE($H-CH_2CH_2OH$) = 100.6 kcal/mol, and BDE(CH_3CH_2O-H) = 104.5 kcal/mol, and values at 298 K of BDE($CH_3CHOH-H$) = 94.8 kcal/mol, BDE($H-CH_2CH_2OH$) = 101.7 kcal/mol, and BDE(CH_3CH_2O-H) = 105.2 kcal/mol. The BDE(O−H) of 105.0 kcal/mol obtained using CBS-Q method[28] differs by 0.2 kcal/mol from our higher level value. The BDE(C−H) in CH_3OH of 95.0 kcal/mol can be compared to the strength of the $C_\alpha-H$ bond of 93.9 kcal/mol in C_2H_5OH. The C−H bond strength is reduced by methyl substitution. As expected, the BDE($C_\beta-H$) in ethanol is substantially larger, 100.6 kcal/mol. The BDE(C_2H_5O-H) = 104.5 kcal/mol indicates a slightly smaller O−H bond strength in ethanol than in methanol (BDE(CH_3O-H) of 104.7 kcal/mol).

The DBOCs to the bond dissociation energy were also calculated. To benchmark our calculations, we calculated the corrections for H_2O to compare with previous work.[84] We obtained 600.3 cm^{-1} for the DBOC of the total energy of water, 2.0 cm^{-1} lower than that of the previous study and a correction of 0.11 kcal/mol for BDE(H−OH), the same value obtained by Ruscic et al.[84] using a CASSCF(7,2)/aVTZ wavefunction. For methanol, we obtained a DBOC to the C−H bond energy of CH_3OH of 0.02 kcal/mol. For ethanol, we found DBOCs to BDE($H-CH_2CH_2OH$) of 0.05 kcal/mol and for BDE($CH_3CH(-H)OH$) of 0.02 kcal/mol. We were unable to evaluate the DBOCs for the O−H bond energies in CH_3OH and CH_3CH_2OH because the presence of the low-lying electronic state. On the basis of the value for the DBOC for the O−H bond in H_2O, we estimate that the correction should be on the order of 0.1 kcal/mol, which is small compared to other errors that could be present. Thus as in the case of the molecular spin−orbit corrections, the DBOCs are also negligible in terms of our estimates of the errors in the calculations.

The calculated gas phase acidity, the proton affinity of the ethoxy anion, $\Delta H_{acidity}(C_2H_5O-H)$ = 378.8 kcal/mol, is in excellent agreement with the literature value of 378.6 ± 0.7 kcal/mol.[16] Ethanol is more acidic than methanol, as expected. The proton affinity of the ethoxy radical is 176.3 kcal/mol (298 K), exhibiting an increase of 8.8 kcal/mol on the radical basicity on substitution of a C_2H_5 group for a CH_3 group (Table 5). This is a larger effect than observed in the corresponding alcohols with PA(CH_3OH) = 180.3 kcal/mol and PA(C_2H_5OH) = 185.6 kcal/mol.[83] The radicals are slightly less basic than the parent alcohols in the gas phase.

Energy Barrier to Cleavage of the C−C Bond of the Ethoxy Radical. As summarized in the Introduction, there is substantial interest in the dissociation process for the β-C−C bond in alkoxy radicals, in part due to the role of this process in atmospheric chemistry. Our best estimate predicts the C−C bond energy in **3** ($^2A''$) to be 9.6 kcal/mol at 0 K. There is an additional energy barrier to dissociation beyond just the bond strength. For comparison, the bond energy to break the $C_\alpha-H$ bond in **3**, generating acetaldehyde, is 15.8 kcal/mol at 0 K. In contrast, the BDE for the C−C bond in ethanol is 87.3 kcal/mol at 298 K, almost an order of magnitude larger.[5] To better understand the fundamental process for breaking the C−C bond in the prototypical alkoxy radical $CH_3CH_2O^•$, we located the **3-TS** for the C−C bond cleavage.

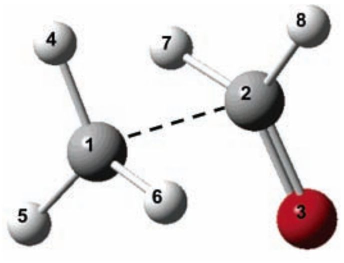

Figure 1. Geometry of the transition state structure **3-TS** for the β-C−C bond scission in 3.

The geometries of **3** ($^2A''$) and **3-TS** were optimized at the MP2 and CCSD(T) methods with both aVDZ and aVTZ basis sets. The calculated bond distances and angles are shown Table 6 and the shape of **3-TS** is illustrated in Figure 1. As expected, the main differences between the MP2 and CCSD(T) results are the breaking C···C and forming C═O bond distances. These are predicted to be longer by CCSD(T), ~0.1 and ~0.03 Å, respectively, relative to those at the MP2 level. Similarly, extension of the basis set at both methods tends to lengthen these distances, but to a much lesser extent by about 0.01 Å. Thus, the aVDZ basis set is providing reasonable geometries for the alkoxy radical and its transition state. The bond angle differences vary by less than 1°. A looser transition state is predicted by CCSD(T). **3-TS** has C_s symmetry as depicted in Figure 1 and a $^2A'$ electronic state, with a geometry close to that of the $H_2CO + CH_3$ fragments. Each of the latter only marginally deviates from planarity. The C1−C2 distance of about 2.1 Å is much longer than the single C−C bond distance of 1.52 Å found in **3**. In contrast, the C1−O3 bond distance of about 1.22 Å in **3-TS** is essentially the same as the C═O double bond distance of 1.21 Å in CH_2O. The imaginary frequencies of 616i and 435i cm^{-1} at the UMP2/aVTZ and CCSD(T)/aVDZ levels, respectively, correspond mostly to dissociation along the C−C bond.

In spite of intensive searching, we were not able to locate a TS for C−C bond cleavage on the $^2A''$ potential energy surface. Single point electronic energies at the CCSD(T)/aVDZ level with the parameters of $^2A'$ **3-TS** show that the $^2A''$ state lies about 40 kcal/mol higher in energy than the $^2A'$ state, and the two corresponding potential energy surfaces are thus well separated from each other. The large energy difference is consistent with the essentially zero value for the molecular spin−orbit energy. The fact that the $^2A''$ state for **3** is fluxional for torsion about the C−C bond means that it is always sampling the ^2A nonsymmetric state. The ^2A state can connect directly to the $^2A'$ transition state **3-TS** so there is no need to invoke a surface crossing between the $^2A''$ and $^2A'$ states and the reaction can occur on a single potential energy surface.

The energy barrier for β-C−C bond scission in **3** ($^2A''$) is predicted to be 17.2 kcal/mol at 0 K and 17.4 kcal/mol at 298 K, on the basis of CCSD(T)/aVTZ geometries (Table 6), CCSD(T)/aVDZ and MP2/aVTZ frequencies (Table S3, Supporting Information), and CCSD(T)/CBS total energies (Table S1, Supporting Information). The uncorrected electronic energy contribution to the barrier height is 19.5 kcal/mol (from Table 2). For comparison purposes, Table 7 lists the energy barriers and reaction energies determined using different levels of theory. The bond energy at the CCSD(T)/aVDZ level is larger by 0.8 kcal/mol as compared to the result at the CBS limit; this

TABLE 7: Comparison of Energy Barrier ($E_0^\ddagger$) and Bond Dissociation Energy for the β-C−C Bond Scission in 3 in kcal/mol

method[a]	$E_0^\ddagger$	BDE(C-C)
CCSD(T)/aVDZ + ZPE[b]	19.39	10.58
CCSD(T)/aVTZ + ZPE[c]	17.98	10.41
CCSD(T)/aVQZ + ZPE[c]	17.62	10.05
CCSD(T)/CBS + ZPE	17.09	9.81
CCSD(T)/CBS + ZPE + additional corrections at 0 K	17.22	9.64
CCSD(T)/CBS + ZPE + additional corrections at 298.15 K	17.43[d]	11.42

[a] Based on scaled CCSD(T)/aVDZ harmonic vibrational frequencies. [b] CCSD(T)/aVDZ geometry. [c] CCSD(T)/aVTZ geometry. [d] This value corresponds to $\Delta H^\ddagger$, not to $E_0^\ddagger$.

difference is 0.6 kcal/mol at the CCSD(T)/aVTZ level. The barriers at the CCSD(T)/aVDZ and aVTZ levels are 2.3 and 0.9 kcal/mol larger, respectively, than the values at CBS limit. The additional corrections beyond the valence energy and the ZPE account for less than 0.15 kcal/mol.

There have been a number of previous theoretical studies of the C−C bond fragmentation as discussed above. Yamada et al.[27] obtained energy barriers of 13.4 and 16.0 kcal/mol (at 0 K), using the CBS-Q and G2 methods, respectively.[26] The CBS-RAD approach led to energy barriers of 15.9 (0 K) and 16.2 (298 K) kcal/mol.[30] These results differ by less than 1 kcal/mol from our best values of 17.2 kcal/mol at 0 K and 17.4 kcal/mol at 298 K.

Given the calculated energy barrier and structural parameters of structures **3** ($^2A''$) and **3-TS**, the temperature-dependency of the canonical rate coefficients for decomposition, k(T), can be evaluated within either the framework of conventional transition state theory (TST) or RRKM theory. For comparison, the entropy of activation, $\Delta S^\ddagger$ at 298 K defined as the difference between S(**3**) and S(**3-TS**), is calculated to be 2.23 cal/(mol·K) using the scaled CCSD(T)/aVDZ data. This value for $\Delta S^\ddagger$ is similar to that of 1.7 cal/(mol·K) at the CBS-RAD level.[30] We initially treated the internal rotation of the methyl group as a vibration. One could include a more rigorous treatment of the internal rotations but previous workers[27] have shown these effects to be negligible. The calculated torsion barrier about the C−C bond is ~2.1, ~2.5, and ~1.4 kcal/mol in **3** ($^2A'$), **3** ($^2A''$), and **3-TS**, respectively. A correction was made on the thermodynamic partition function to account for hindered rotation following the method of Pitzer and Gwinn[85] as implemented by Ayala and Schlegel.[86] Our calculations treating the internal rotation in **3** ($^2A'$) show a change of 0.04 kcal/mol on the ZPE and 0.25 cal/(mol·K) on S as compared to the treatment of the internal rotation as a harmonic vibration. The use of scaled frequencies increases the vibrational component of the molecular entropy of **3** and **3-TS** by less than 0.1 cal/(mol·K) but this essentially cancels in $\Delta S^\ddagger$.

We first evaluated the high-pressure rate constant using the conventional TST approximation.[42] The thermal rate constant in the thermodynamic formulation is given by

$$k_\infty(\mathrm{TST}) = \frac{k_B T}{h} \exp\frac{\Delta S^\ddagger}{R} \exp\frac{-\Delta H^\ddagger}{RT} \tag{7}$$

and the high-pressure limit pre-exponential factor is thus given by $A = (k_B T/h)\exp(\Delta S^\ddagger/R)$. Note that the E_a of the Arrhenius expression from TST and $\Delta H^\ddagger$ are related by $E_a = \Delta H^\ddagger + RT$ for a unimolecular process.[42] Our calculated zero-point-corrected barrier height $E_0^\ddagger$ is 17.4 kcal/mol which results in $\Delta H^\ddagger = 17.4$ kcal/mol and $\Delta S^\ddagger = 2.23$ cal/(mol·K) at 298 K. This yields $\log(A) = 13.28$, $E_a = 18.0$ kcal/mol and $k_\infty = 3.2$ s^{-1} at 298 K.

With the same TST approach with $\Delta H^\ddagger = 16.2$ kcal/mol and $\Delta S^\ddagger = 1.67$ cal/(mol·K), Rauk et al.[30] obtained $\log(A) = 13.60$, $E_a = 16.8$ kcal/mol, and $k_\infty = 19$ s^{-1} at 298 K. This value for k_∞ is 5.9 times larger than our value, consistent with their lower value for E_a (1.2 kcal/mol relative to our value). Sonnitz and Zellner[40] used RRKM theory[41] with geometrical and energetic inputs from modified G2 calculations with $E_0^\ddagger = 17.33$ kcal/mol resulting in $E_a = 17.94$ kcal/mol, $\log(A) = 13.47$, and $k = 2.43$ s^{-1} at 300 K. Their value is in good agreement with our value for k_∞.

Previous experimental kinetic studies[33,34,35,40] reported values for $\log(A)$ ranging from 13.0 to 15.7, and E_a from 16.8 to 22.0 kcal/mol. In the above calculations, we have not included in our TST treatment any corrections for quantum mechanical tunneling, even though a heavy-atom tunneling effect may be present. Due to the presence of a barrier between the reactant and the dissociated products, higher level vibrational states of the reactant can tunnel through the barrier leading to a heavy-atom tunneling effect. We note that this effect occurs because of a barrier of finite height and width between the reactants and products. The dominant motion for dissociation is C−C bond stretching leading to the concept of heavy atom tunneling. An estimate of the tunneling effect Q_{tunnel} can be calculated from the Wigner expression (eq 8),[42,87] which just requires the

$$Q_{\mathrm{tunnel,W}}(T) = 1 + \frac{1}{24}\left(\frac{h\omega_i}{k_B T}\right)^2 \tag{8}$$

imaginary frequency ω_i for motion along the reaction path at the transition state structure. An improved approximation for Q_{tunnel}, which incorporates not only the imaginary frequency but also the energy barrier $\Delta H^\ddagger$ and reaction energy ΔH_R, has been derived by Skodje and Truhlar[88] and is given in eq 9 with

$$Q_{\mathrm{tunnel,ST}}(T) = \frac{\beta\pi/\alpha}{\sin(\beta\pi/\alpha)} - \frac{\beta}{\alpha - \beta}\exp[(\beta - \alpha)(\Delta H^\ddagger - \Delta H_R)] \tag{9}$$

$\beta = k_B T$ and $\alpha = 2\pi/h\omega_i$ (this expression is valid only for $\alpha > \beta$). Our calculated imaginary frequencies for **3-TS** are $\omega_i = 435i$ (CCSD(T)/aVDZ) and $\omega_i = 616i$ cm^{-1} (MP2/aVTZ). From these values, we obtain values for $Q_{\mathrm{tunnel,W}}$ at 298 K of 1.18 and 1.37, from eq 8 with 435i and 616i, respectively. The use of eq 9 leads to slightly larger values for $Q_{\mathrm{tunnel,ST}}$(298 K) of 1.21 and 1.49. We are also interested in the effect of tunneling on atmospheric rate processes. We use an average temperature for the troposphere of 270 K and obtain $Q_{\mathrm{tunnel,W}}$(270 K) values of 1.22 and 1.45, and $Q_{\mathrm{tunnel,ST}}$(270 K) values of 1.27 and 1.65, with the CCSD(T) and MP2 frequencies, respectively. Our results provide only an estimate of the tunneling correction but show that this will be a non-negligible correction to thermal rates at temperatures below 1000 K, especially at or below room temperature (a table of Q_{tunnel} factors as a function of the temperature is given in Table S6 of the Supporting Information).

The tunneling correction will be important in low-temperature oxidation processes such as those in the atmosphere but is unlikely to be very important in higher temperature processes such as those occurring under hydrocarbon combustion conditions in engines. Using the tunneling correction from eq 9, our predicted thermal rate constants increase from k_∞(298 K) = 3.2 s^{-1} (without tunneling correction) to k(298 K) = 3.9 s^{-1} and 4.8 s^{-1} (with the CCSD(T) and MP2 imaginary frequencies, respectively). Both rate constants are in excellent agreement

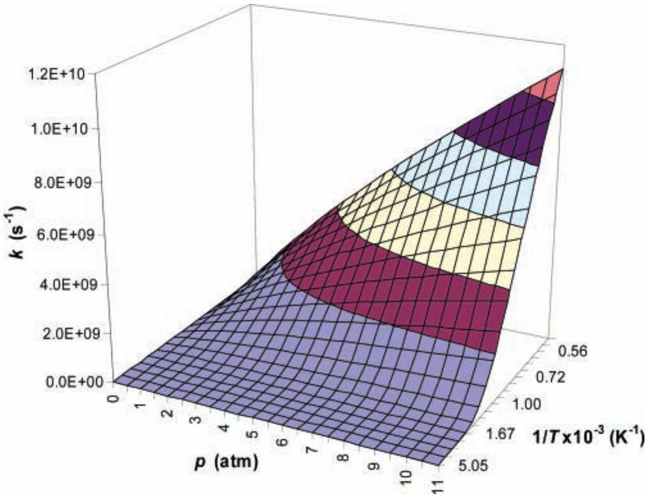

Figure 2. 3-D plot of the rate coefficients k of the for the β-C−C bond scission in **3** using the RRKM method with N_2 as the bath gas in the temperature range (T) 200−2000 K and pressure range (p) 0.1−8360 Torr. Tunneling corrections are not included.

with the recent experimental value of 5.2 s^{-1} by Caralp et al.[35] Our calculated value and the experimental value obtained by Caralp at 298 K, clearly differ from the review value of Baulch et al. of 1.9×10^{-2} s^{-1},[89] the value of 1.3×10^{-1} s^{-1} in the review of Heicklen,[90] Choo and Benson's value of 7.6×10^{-2} s^{-1},[91] and Baldwin et al.'s estimated value of 6.5×10^{-3} s^{-1}.[92] These values are all far too low. We can also compare to the higher temperature values of Batt at 400[33a] and 450[33e] K and of Leggett and Thynne[33d] at 422 K. Our calculated values, including tunneling with the CCSD(T) imaginary frequency, are $k = 8.5 \times 10^3$ and 1.1×10^5 s^{-1} at 400 and 450 K, which are a factor of 5.7 and 3.7 times higher than the respective values of Batt of 1.5×10^3 and 3.0×10^4 s^{-1} at the two temperatures. The calculated value of $k = 2.8 \times 10^4$ s^{-1} at 422 K does not support the value of $k = 5.3$ s^{-1} at 422 K from Leggett and Thyme. Using 270 K as a representative temperature for the atmosphere, we predict $k = 1.3 \times 10^{-1}$ s^{-1} (without tunneling correction) and $k = 1.7 \times 10^{-1}$ and 2.2×10^{-1} s^{-1} (with the tunneling corrections from the CCSD(T) and MP2 frequencies respectively).

We also used RRKM theory[41] to predict the rate constants using the rate expression 10, where σ is the symmetry number. Evaluation of the sum ($N^{\ddagger}$) and density (ρ) of states was carried

$$k_{\mathrm{uni}} = \frac{\sigma}{h}\left[\frac{N^{\ddagger}(E - E_0)}{\rho(E)}\right] \tag{10}$$

out using the KHIMERA program.[93] We show the rate constant as a function of T and p for the range of temperatures from 200 to 2000 K and pressures from 0.1 to 8360 Torr in Figure 2. Again, we used the CCSD(T)/aVTZ geometries and CCSD(T)/aVDZ frequencies combined with CCSD(T)/CBS total electronic energies. For this range of T and p with N_2 as the collision gas, the calculated data can be fit to the general expression

$$k(T,p)_{\mathrm{ethoxy\ radical}} = 1.26 \times 10^9 p^{0.793} \exp\left(\frac{-15.5}{RT}\right) \tag{11}$$

At 298 K and 760 Torr, $k = 2.7$ s^{-1}, without tunneling and $k = 3.2$ s^{-1}, with the CCSD(T) value using the Skodje and Thrular tunneling expression $Q_{\mathrm{tunnel,ST}}$ applied as a multiplicative factor after the RRKM calculation. At a high pressure of ~8000 Torr, the decomposition thermal rate coefficient is $k = 3.0$ s^{-1} at 298 K, using N_2 as the bath gas, comparable to our TST result for $k_\infty = 3.2$ s^{-1} (without a tunneling correction) and 1 order of magnitude larger than previous RRKM predictions.[40]

Conclusion

The enthalpies of formation for methanol and ethanol, and their corresponding radicals were reevaluated using coupled-cluster theory CCSD(T) calculations, extrapolated at the CBS limit. For methanol, the two ($CH_3O^{\bullet}$) radicals and ethanol, theoretical results agree within ±0.5 kcal/mol with respect to available experimental data. On the basis of the results for CH_3OH, we estimate that our calculated values for CH_3CH_2OH are good to ±0.8 kcal/mol and recommend the following values for the three ($C_2H_5O^{\bullet}$) radicals: (a) heats of formation at 0 K $\Delta H_{f,0}(\mathbf{1}) = -9.8$ kcal/mol, $\Delta H_{f,0},(\mathbf{2}) = -3.1$ kcal/mol, and $\Delta H_{f,0}(\mathbf{3}) = 0.8$ kcal/mol; (b) heats of formation at 298 K $\Delta H_{f,298}(\mathbf{1}) = -13.1$ kcal/mol, $\Delta H_{f,298}(\mathbf{2}) = -6.2$ kcal/mol, and $\Delta H_{f,298}(\mathbf{3}) = -2.7$ kcal/mol; (c) bond dissociation energies of ethanol at 0 K BDE($CH_3CHOH-H$) = 93.9 kcal/mol, BDE($H-CH_2CH_2OH$) = 100.6 kcal/mol, and BDE(CH_3CH_2O-H) = 104.5 kcal/mol; (d) bond dissociation energies of ethanol at 298 K BDE($CH_3CHOH-H$) = 94.8 kcal/mol, BDE($H-CH_2CH_2OH$) = 101.7 kcal/mol, and BDE(CH_3CH_2O-H) = 105.2 kcal/mol. The bond energy at 0 K for β-C−C bond scission in the ethoxy radical (**3**) is 9.6 kcal/mol. There is a zero-point-corrected energy barrier of 17.2 kcal/mol, at 0 K, for this dissociation process. At 298 K, our best value for the high-pressure limit thermal (Arrhenius) rate coefficient from transition state theory of $k_\infty = 3.9$ s^{-1} is close to the most recent kinetic result of 5.2 s^{-1}.[35] Using RRKM theory, we obtain a general rate expression of $k(T,p) = 1.26 \times 10^9 p^{0.793} \exp(-15.5/RT)$ s^{-1} in the temperature range (T) from 198 to 1998 K and pressure range (p) from 0.1 to 8360.1 Torr with N_2 as the collision partner which gives k(298 K, 760 Torr) = 2.7 s^{-1}, without tunneling and $k = 3.2$ s^{-1} with the tunneling correction.

Acknowledgment. We are grateful to Dr. Shenggang Li for his help with some of the calculations. We thank B. Ruscic for calculating the temperature dependence of $\Delta H_f(CH_3CH_2O)$ with the inclusion of the A′ excited state. Funding provided in part by the Department of Energy, Office of Energy Efficiency and Renewable Energy, under the Hydrogen Storage Grand Challenge, Solicitation No. DE-PS36-03GO93013. This work was done as part of the Chemical Hydrogen Storage Center. This work was supported in part by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE), under grant no. DE-FG02-03ER15481 (catalysis center program). D.A.D. is indebted to the Robert Ramsay Endowment of the University of Alabama. M.T.N. thanks the Flemish FWO-Vlaanderen for partly supporting his sabbatical leave at the University of Alabama.

Supporting Information Available: Optimized geometries (**Z** matrix), calculated vibrational frequencies and comparison to experiment, total CCSD(T) energies (E_h) as a function of basis set extrapolated to the complete basis set limit, zero-point energy corrections, tunneling corrections. This material is available free of charge via the Internet at http://pubs.acs.org.

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