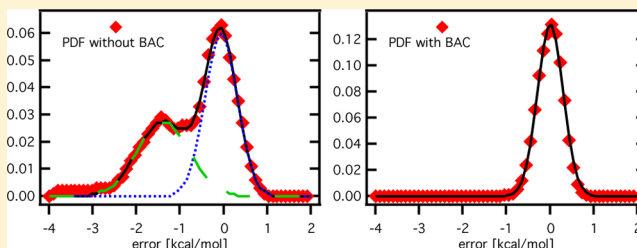


Database of Small Molecule Thermochemistry for Combustion

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S Supporting Information

ABSTRACT: High-accuracy ab initio thermochemistry is presented for 219 small molecules relevant in combustion chemistry, including many radical, biradical, and triplet species. These values are critical for accurate kinetic modeling. The RQCISD(T)/cc-pV ∞ QZ//B3LYP/6-311++G(d,p) method was used to compute the electronic energies. A bond additivity correction for this method has been developed to remove systematic errors in the enthalpy calculations, using the Active Thermochemical Tables as reference values. On the basis of comparison with the benchmark data, the 3 σ uncertainty in the standard-state heat of formation is 0.9 kcal/mol, or within chemical accuracy. An uncertainty analysis is presented for the entropy and heat capacity. In many cases, the present values are the most accurate and comprehensive numbers available. The present work is compared to several published databases. In some cases, there are large discrepancies and errors in published databases; the present work helps to resolve these problems.



■ INTRODUCTION

The availability of accurate thermochemical parameters is critical for many applications, including modeling of combustion chemistry. To maintain thermodynamic consistency within a chemical kinetic mechanism, the standard practice in the combustion community is to specify the rate coefficient for a reaction in one direction (e.g., the forward rate constant) and then compute the reverse rate coefficient from the equilibrium constant.¹ Although this approach enforces thermodynamic consistency, the accuracy of the reverse rate coefficient is limited by the accuracy of the free energy of reaction: an error of 5 kcal/mol in Gibbs free energy will result in an equilibrium constant that is off by a factor of 12 at 1000 K, and the effect is even larger at lower temperatures. Consequently, it is essential that the relevant thermochemistry—enthalpy, entropy, and heat capacity—for each species be known as accurately as possible. Furthermore, the scope of the need for accurate thermochemical parameters is large; depending on conditions of interest (including factors such as composition, temperature, and pressure), it is conceivable that accurate thermochemical parameters for any of the thousands of intermediates, reactants, or products are crucial to accurate modeling of the system as a whole.

Although databases are available that cover a large number of compounds of interest, such as those by NIST,² Baulch et al.,³ PrIme,⁴ Active Thermochemical Tables (ATcT),⁵ and the Third Millennium Thermodynamic Database (TMTD),⁶ even these large databases are not comprehensive and omit many compounds of interest. Most existing databases are unevaluated compilations, so inaccuracies in the original article are often republished, and errors may be passed from one database to the next. A careful review of the literature and/or the application of new methodologies is often warranted.

Here we present an application of an QCISD(T) quantum chemistry approach to calculating thermochemical parameters

for over 200 molecular species of interest in combustion chemistry. The results are presented here in the spirit of similar thermochemical compendiums using other ab initio methods for other molecular species ensembles (e.g., refs 7–9). QCI is a truncation method for the full Configuration Interaction (CI), with singly (S) and doubly (D) excited determinants and a perturbative treatment of the triple (T) excitations, in which the higher-order terms are quadratic (Q) in their expansion coefficients.¹⁰ In their review of low-temperature oxidation chemistry, Zádor et al.¹² cite unpublished work from Senosian, Klippenstein, and Miller in which QCISD(T)/cc-pV ∞ QZ//B3LYP/6-311++G(d,p) calculations were compared with 17 species in the test set of hydrogen abstraction reactions of Lynch et al.;¹¹ it was found that the QCISD(T) method performed slightly better than the more expensive CCSD(T) calculations in calculating the barrier heights. The QCISD(T) electronic structure calculations used in the present work are essentially equivalent to those carried out by Senosian, Klippenstein, and Miller, and this method was chosen as an appropriate compromise between accuracy and cost.

■ COMPUTATIONAL METHODS

For each species in the library, the $\sim 3^n$ possible conformers, where n is the number of torsional modes, were calculated using the CBS-QB3 method.¹³ The lowest energy conformer was selected, and this geometry was reoptimized using the B3LYP functional with the 6-311++G(d,p) basis set. RQCISD(T)/cc-pVTZ and RQCISD(T)/cc-pVQZ energies were calculated at

Received: April 20, 2012

Revised: August 7, 2012

Published: August 8, 2012

the resulting DFT geometries. All DFT calculations were done using Gaussian03.¹⁴ All MP2 and RQCISD(T) calculations were done using MOLPRO.¹⁵ To avoid spin contamination, all calculations were spin restricted (e.g., RHF for closed-shell species and ROHF for open-shell species). For open shell species, the MOLPRO initial guess for the α and β spin orbitals in the ROHF calculation is sometimes inaccurate, and the resulting post-Hartree–Fock calculations were off by ~ 30 kcal/mol. The ROHF calculations were therefore preceded with a UHF calculation, which provided a better guess for the open-shell spin restricted calculation. Additionally, for molecules with an Abelian point group other than C1, the correct symmetry orientation was provided explicitly in the MOLPRO calculations. The QCISD(T) complete basis set (CBS) limit was extrapolated from the triple and quadruple- ζ basis set calculations assuming an inverse power law:^{16,17}

$$E_{\text{QCISD}/\infty\text{QZ}} = E_{\text{QCISD}/\text{QZ}} + (E_{\text{QCISD}/\text{QZ}} - E_{\text{QCISD}/\text{TZ}}) \frac{4^4}{5^4 - 4^4} \quad (1)$$

For some of the largest species (denoted with a superscript “a” in Table 3) the QCISD(T)/cc-pVQZ calculations were computationally prohibitive. Instead, restricted QCISD(T)/cc-pVDZ and QCISD(T)/cc-pVTZ energies were calculated at the DFT geometries, and the CBS limit energy was estimated from extrapolations of the cc-pVDZ and cc-pVTZ results. The MP2 method was then used to correct for the difference in cc-pVDZ, cc-pVTZ and cc-pVTZ, cc-pVQZ based extrapolations, yielding:¹⁸

$$E_{\text{QCISD}/\infty(\text{Q})\text{Z}} = E_{\text{QCISD}/\text{TZ}} + (E_{\text{QCISD}/\text{TZ}} - E_{\text{QCISD}/\text{DZ}}) \frac{3^4}{4^4 - 3^4} + E_{\text{MP2}/\text{QZ}} + (E_{\text{MP2}/\text{QZ}} - E_{\text{MP2}/\text{TZ}}) \frac{4^4}{5^4 - 4^4} - E_{\text{MP2}/\text{TZ}} - (E_{\text{MP2}/\text{TZ}} - E_{\text{MP2}/\text{DZ}}) \frac{3^4}{4^4 - 3^4} \quad (2)$$

With the exception of free rotors, resonantly stabilized radicals, and cyclic structures, all single bonds between heavy atoms were treated as one-dimensional hindered internal rotors. For each torsional mode the barriers for internal rotation were calculated by a relaxed scan in 10° increments at the B3LYP/6-31+G(d,p) level, and the rotational potential was fit to a Fourier series. If the maximum barrier for internal rotation was less than 0.5 kcal/mol, which corresponds to $k_B T$ of ~ 250 K, the rotor was treated as a free rotor. For species in which a radical site is adjacent to a double bond (e.g., allyl) the unpaired electron is delocalized by the neighboring π -orbitals. Because the π -orbital resonance is destroyed in rotating the $-\text{CH}_2^\bullet$ moiety relative to the double-bond, this torsional mode has a high barrier to rotation. Consequently, the single bonds in allylic radicals are not treated as hindered rotors. This assumption was tested for allyl, and the heat capacity for the RRHO and hindered rotor models agreed to within two percent for $300 \leq T \leq 2500$ K. To reduce the ambiguity regarding low-frequency vibrations and the corresponding torsional modes, the projection of the B3LYP/6-311+G(d,p) force-constant matrix was removed along the vectors corresponding to changing each dihedral angle while holding the other internal coordinates fixed. This matrix was then diagonalized, which separated the rigid-rotor harmonic-oscillator frequencies from the torsional modes.¹⁹ This procedure was

applied at the global equilibrium geometry. For all hindered rotors, it is assumed that the torsional modes can be separated and approximated by a one-dimensional rotation. A Hamiltonian is formed from this potential, and the corresponding 1D Schrödinger equation is solved for the energy levels, ϵ_j . The partition function is calculated by summing over the energy levels, $Q = \sum_j \exp[-\epsilon_j/k_B T]$, and the enthalpy, entropy, and heat capacity are computed accordingly. The effective moment of inertia for each rotor was $I^{(2,3)}$, evaluated at the equilibrium geometry. We note that a variety of methods have been proposed for handling the coupling between hindered rotors and with other motions. Standard statistical thermodynamic models were used for the remaining degrees of freedom.

The atomization energy of the molecule, $\sum D_0$, is computed using eq 3:

$$\sum D_0 = \sum_{j=\text{H,C,O}} x_j E_{0,j} - E_0 - E_{\text{ZPE}} \quad (3)$$

where x_j is the number of atom type j in the molecule, $E_{0,j}$ is the calculated total electronic energy for that atom type including spin–orbit corrections,²⁰ E_0 is the RQCISD(T)/cc-pV ∞ QZ electronic energy of the molecule, and E_{ZPE} is the B3LYP/6-311+G(d,p) zero-point energy. The zero-point energy was computed by harmonic normal-mode analysis including all $3N$ degrees of freedom, with all frequencies scaled by 0.99. The standard-state heat of formation, $\Delta_f H_{298\text{ K}}^0$ is computed from the atomization energy and the experimental heats of formation of the atoms, as in eq 4:

$$\Delta_f H_{298\text{ K}}^0 = \sum_{j=\text{H,C,O}} x_j (\Delta_f^{\text{exp}} H_{0\text{ K},j}^0 - [H_j^0(298\text{ K}) - H_j^0(0\text{ K})]) - \sum D_0 + [H(298\text{ K}) - H(0\text{ K})] \quad (4)$$

where $\Delta_f^{\text{exp}} H_{0\text{ K},j}^0$ is the experimental enthalpy of formation for the atoms at zero Kelvin, and the two terms in square brackets are the enthalpy corrections for the atoms and molecules, respectively, from 0 to 298 K. The calculated total electronic energies and the experimental enthalpy of formation for the atoms used in eqs 3 and 4 are listed in Table 1.

Table 1. Experimental Enthalpies of Formation and Calculated Total RQCISD(T) Energies for H, C, and O Atoms, in kcal/mol (Experimental values from NIST-JANAF²¹)

element	$E_{0,j}$	$\Delta_f^{\text{exp}} H_{0\text{ K},j}^0 - [H_j^0(298\text{ K}) - H_j^0(0\text{ K})]$
H	−313.78	50.62
C	−23713.95	169.73
O	−47067.78	57.95

The calculation of the thermochemistry was performed using the software CanTherm.²² The thermochemical parameters were calculated in 10°C increments from 300 to 3000 K. The results were then fit to the standard 14 parameter NASA polynomial. The results for the 219 molecules are summarized in Table 3.

Included in Table 3 is the RQCISD(T)/cc-pVQZ T1 diagnostic.²³ The T1 diagnostic is a measure of the importance of multireference effects. For closed shell species with a T1 diagnostic less than ~ 0.02 , and for radicals with a T1 diagnostic less than ~ 0.03 , the RQCISD(T) energies are expected to be accurate to ± 1 kcal/mol, and multireference calculations are unnecessary.²⁴ For the vast majority of species considered, a

single-reference wave function is sufficient. The largest exceptions are $^1\text{C}_2$ ($T1 = 0.041$) and ketylperoxy ($T1 = 0.043$). Several peroxy radicals have a $T1$ diagnostic between 0.030 and 0.037, with a general trend based upon size and degree of saturation. Smaller peroxy radicals and peroxy radicals with unsaturated bonds have a larger $T1$ diagnostic. For example, HOO^\bullet and $\text{CH}_3\text{OO}^\bullet$ have $T1 = 0.037$ and 0.036 , respectively, whereas normal $\text{C}_3\text{H}_7\text{OO}^\bullet$ and iso- $\text{C}_3\text{H}_7\text{OO}^\bullet$ have $T1 = 0.014$. Similarly, the $T1$ diagnostic increases with the proximity of the peroxy group to unsaturated bonds: in (2-formylethyl)peroxy ($\text{O}=\text{CHCH}_2\text{CH}_2\text{OO}^\bullet$) the peroxy group and the double bond are separated by two C—C bonds, in allylperoxy ($\text{CH}_2=\text{CHCH}_2\text{OO}^\bullet$) by one C—C bond, and in propen-1-peroxy ($\text{CH}_3\text{CH}=\text{CHOO}^\bullet$) they are adjacent; the corresponding $T1$ diagnostics are 0.013, 0.030, and 0.033, respectively. These trends suggest some interaction between the peroxy moiety and the π orbitals, and multireference methods are recommended if the application requires tighter uncertainty for these species.

BOND ADDITIVITY CORRECTION

To assess the accuracy of the RQCISD(T)/cc-PV ∞ QZ//B3LYP/6-311++G(d,p) method (hereafter “QCI method” for simplicity), the standard-state heats of formation were compared with the Active Thermochemical Tables (ATcT).⁵ A list of the 62 species in common can be found in Table S. A cumulative distribution function (CDF) was determined from the difference in $\Delta_f H_{298}^0$ between the ATcT and the present work. The CDF was interpolated onto an evenly spaced

grid of 0.1 kcal/mol increments. The probability distribution function (PDF) was computed from the interpolated CDF using a finite-difference approximation (fourth-order central difference). The PDF and CDF are presented in panels a and c of Figure 1, respectively. As seen in Figure 1a, the PDF is easily represented by the sum of two normal distributions, with one distribution centered at -0.06 kcal/mol and the second distribution centered at -1.38 kcal/mol.

The presence of two distinct distributions suggests a systematic error in the QCI method, the source of which can be determined from the corresponding CDF. All species that contain double or triple carbon–carbon bonds are shown in Figure 1c with solid squares; the remaining species are shown with open circles. As can be seen in Figure 1c, the QCI method overestimates the heat of formation for species with $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bonds, with an average error of roughly 1.4 kcal/mol.

A bond additivity correction (BAC) was developed to remove these and any other systematic errors in bond type. For each of the 62 species, the following eight bond types were tallied: C—H, C—C, C=C, C \equiv C, O—H, C—O, C=O, and O—O. The resulting BAC values are presented in Table 2. The CDF and PDF were recomputed using the BAC. These results are shown in Figure 1d and Figure 1b, respectively. The BACs effectively remove the systematic error in the C=C and C \equiv C bonds. The error in $\Delta_f H_{298}^0$ between the QCI+BAC and the ATcT are between -0.56 and $+0.38$ kcal/mol, with a mean error of 0.00 kcal/mol and standard deviation of 0.29 kcal/mol.

For many resonantly stabilized radicals, the two Lewis structures have different bond types. Application of the BAC is

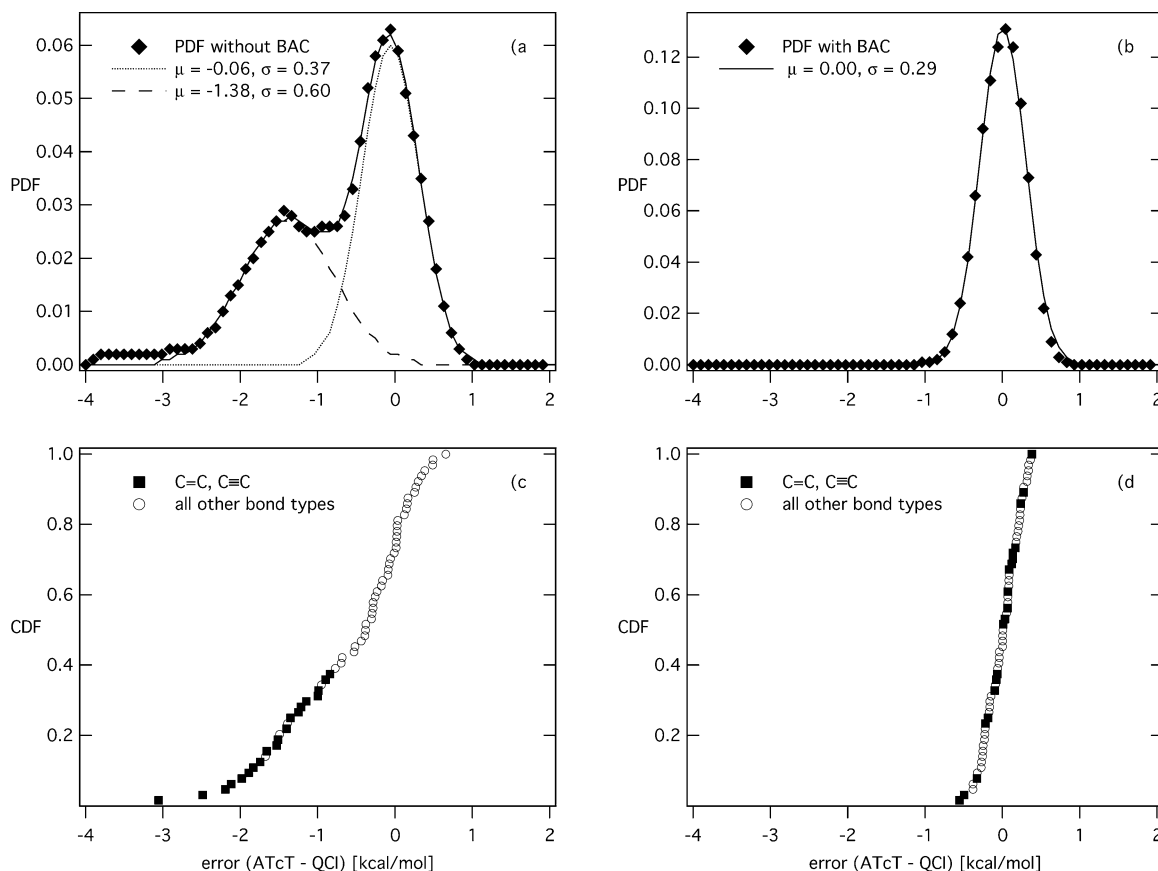


Figure 1. Bond additivity correction. (a) Probability distribution function for the error in the standard-state heat of formation, without BAC. The solid line is the sum of the dotted and dashed lines. (b) Probability distribution function for the error in the standard-state heat of formation, with BAC. (c, d) Cumulative distribution function for the error in the standard-state heat of formation, without BAC and with BAC, respectively.

Table 2. Bond Additivity Correction

bond type	correction [kcal/mol]
C—H	−0.03
C—C	−0.36
C=C	−0.96
C≡C	−1.41
O—H	0.21
C—O	0.09
C=O	0.11
O—O	−0.58

therefore ambiguous. To resolve this ambiguity, the singularly occupied molecular orbital (SOMO) was viewed for each resonantly stabilized radical. In most cases, the location of the spin in the SOMO's was unambiguous, and the corresponding Lewis structure was chosen for the BAC correction. The notable exception was propargyl. The BAC was computed for both Lewis structures for propargyl (e.g., $\bullet\text{CH}=\text{C}=\text{CH}_2$ and $\text{CH}\equiv\text{C}-\text{CH}_2\bullet$). The structure with the more negative BAC, $\text{BAC}_{\bullet\text{CH}=\text{C}=\text{CH}_2} = -2.01$ kcal/mol, was selected. This result was also in better agreement with the ATcT. For each resonantly stabilized radical in Table 3, both Lewis structures are presented. The Lewis structure used for the BAC is always listed first.

RESULTS

The computed standard-state enthalpy of formation, entropy, and heat capacity at seven temperatures are presented in Table 3.

Uncertainty Analysis. As reported in the section on Bond Additivity Correction, the mean error in the standard-state enthalpy of formation between the present work at the ATcT for was 0.00 kcal/mol, with a standard deviation of 0.29 kcal/mol. On the basis of these results, the uncertainty in the enthalpy in Table 3 corresponds to the 3σ uncertainty, or 0.9 kcal/mol. For the 62 species in common between the ATcT and this work, the 3σ uncertainty was replaced by the absolute difference in $\Delta_f H_{298}^0$ plus the stated uncertainty in the ATcT database. In many cases, the result was as small as 0.1 kcal/mol.

Owing the absence of benchmark values for entropy and heat capacity, the quantification of uncertainty for these properties is more complicated. First, the present work assumes that each molecule can be approximated as a rigid-rotor harmonic oscillator (with the previously noted exception for 1D hindered internal rotation), and that all degrees of freedom in the partition functions are separable and independent. Although these assumptions are common practice in statistical thermodynamics, a rigorous uncertainty quantification should address the error resulting from the exclusion of coupling between (and within) the rotational, vibrational, and/or electronic partition functions. Some special effects, such as the coupling between rotation and spin in OH^{25} or the Jahn–Teller distortion in CH_3O^{26} have been addressed previously. The significance of mode–mode coupling and other ubiquitous anharmonic behavior is considerably more difficult to assess.

Sharma et al. analyzed the coupling between internal rotors for hydroperoxylalkylperoxy radicals (e.g., species 104, 189–191).¹⁹ For these species, the conformer with the lowest energy is a quasi-cyclic structure in which the oxygen-centered radical forms a hydrogen bond with the OOH moiety. The hydrogen bonding stabilizes the species by roughly 2 kcal/mol relative to the straight-chain conformer, but it also increases the potentials for internal rotation by nearly a factor of 2, thereby confining the conformer to a narrow well in the multidimensional potential

energy surface. At lower internal energies the structure remains quasi-cyclic; once the internal energy is sufficient to break the hydrogen bonding, the individual torsional barriers decrease, and the species can sample a significantly larger conformational space. This behavior cannot be replicated by a partition function consisting of separable 1D internal rotors, because a realistic partition function would need to take into consideration this multidimensional mode–mode coupling. The standard-state entropy for species 189 was reported by Sharma et al. to be 103 cal/(mol K), which includes the mode–mode coupling for internal rotation. This value is 5 cal/(mol K) greater than the present work. For species 104, 190, and 191, the error is smaller (1, 1, and 0 cal/(mol K), respectively), because fewer torsional modes in the quasi-cyclic structure are affected by the hydrogen bonding.

Although a rigorous investigation of anharmonicity under combustion conditions is urgently needed, such work is beyond the scope of this paper. Instead, we limit our attention to how uncertainty in the ro-vibrational parameters (i.e., vibrational frequencies, hindered-rotor potentials, and moments of inertia) is propagated through the separable, independent partition functions into uncertainty in the entropy and heat capacity. Even this task is not straightforward, because these parameters are correlated in a manner that is difficult to predict a priori. As evidenced by the bond additivity correction, the geometry optimization method may consistently underestimate (or overestimate) the length of certain bond types, which would increase (decrease) the corresponding vibrational modes and rotational barrier heights and decrease (increase) the external moments of inertia.

Two sets of calculations were performed to ascertain the uncertainty in the entropy and heat capacity. For each species, the upper/lower error bounds for the rovibrational parameters were assumed to be $\pm 10\%$ for the vibrational frequencies, $\pm 20\%$ for the hindered rotor potentials, and $\pm 5\%$ for the external moments of inertia:

$$\nu_j = (0.9 + 0.2x)\nu_{j,0} \quad (\text{Sa})$$

$$V_k(\phi) = (0.8 + 0.4x)V_{k,0} \quad (\text{Sb})$$

$$I_x = (0.95 + 0.1[1 - x])I_{x,0} \quad (\text{Sc})$$

where ν_j corresponds to one of the $3N - 6 - N_{\text{HR}}$ vibrational modes, $V_k(\phi)$ corresponds to the rotational potential for one of the N_{HR} torsional modes, I_x corresponds to one of the three external moments of inertia, the subscript 0 refers to the nominal value of the parameter, and $x \in [0, 1]$. In the first set of calculations, called “low”, $x = 0$ for all parameters in eq 5; in the second set, “high”, $x = 1$. Thus, these calculations represent a “worst-case” scenario in which all the rovibrational parameters are tightly correlated and at their maximum error. The uncertainties for the entropy and heat capacity presented in Table 3 are the average of this worst-case scenario: $[\text{high} - \text{low}]/2$.

To relate the uncertainties in Table 3 to a standard deviation, two different Monte Carlo uncertainty analyses were performed for ten different species. In the first Monte Carlo analysis, the $3N - 3$ rovibrational parameters were assumed to be completely uncorrelated, and a new random number x was assigned to each parameter. In the second Monte Carlo analysis, the $3N - 3$ parameters were assumed to be completely correlated, and the same random number x was assigned for all parameters. This process was repeated 5000 times for each species and for both

Table 3. Enthalpy, Entropy, Heat Capacity, and T1 Diagnostic



No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
1	H_2	H_2	0.0 ± 0.0	31.1 ± 0.1	6.9 ± 0.0	6.9 ± 0.0	6.9 ± 0.0	7.0 ± 0.0	7.0 ± 0.0	7.1 ± 0.1	7.5 ± 0.1	0.006
2	CH	CH (doublet)	142.3 ± 0.2	43.6 ± 0.1	6.9 ± 0.0	7.0 ± 0.0	7.0 ± 0.0	7.1 ± 0.1	7.3 ± 0.1	7.5 ± 0.1	8.1 ± 0.1	0.009
3	$^1\text{CH}_2$	CH_2 (singlet)	102.5 ± 0.1	45.1 ± 0.2	8.1 ± 0.1	8.3 ± 0.1	8.6 ± 0.2	9.0 ± 0.2	9.8 ± 0.3	10.5 ± 0.3	11.8 ± 0.3	0.009
4	$^3\text{CH}_2$	CH_2 (triplet)	93.8 ± 0.3	46.6 ± 0.2	8.3 ± 0.1	8.7 ± 0.1	9.0 ± 0.2	9.3 ± 0.2	9.9 ± 0.2	10.5 ± 0.3	11.7 ± 0.3	0.012
5	CH_3	methyl	35.2 ± 0.2	46.4 ± 0.3	9.4 ± 0.2	10.1 ± 0.3	10.9 ± 0.4	11.6 ± 0.4	12.9 ± 0.5	14.0 ± 0.5	16.2 ± 0.5	0.005
6	CH_4	methane	-17.6 ± 0.3	44.4 ± 0.2	8.5 ± 0.3	9.6 ± 0.5	11.0 ± 0.7	12.4 ± 0.8	14.9 ± 0.9	17.0 ± 0.9	20.5 ± 0.8	0.008
7	OH	OH	8.9 ± 0.1	43.9 ± 0.1	6.9 ± 0.0	6.9 ± 0.0	7.0 ± 0.0	7.0 ± 0.0	7.1 ± 0.1	7.2 ± 0.1	7.7 ± 0.1	0.007
8	H_2O	H_2O	-58.0 ± 0.2	45.0 ± 0.2	8.0 ± 0.0	8.2 ± 0.1	8.4 ± 0.1	8.6 ± 0.2	9.2 ± 0.2	9.7 ± 0.3	11.0 ± 0.3	0.007
9	CO	CO	-26.3 ± 0.1	47.1 ± 0.1	7.0 ± 0.0	7.0 ± 0.0	7.1 ± 0.1	7.2 ± 0.1	7.6 ± 0.1	7.9 ± 0.1	8.3 ± 0.1	0.019
10	HCO	HCO	10.2 ± 0.2	53.5 ± 0.2	8.3 ± 0.1	8.7 ± 0.2	9.2 ± 0.3	9.7 ± 0.3	10.6 ± 0.3	11.3 ± 0.3	12.5 ± 0.2	0.026
11	formaldehyde	formaldehyde	-26.2 ± 0.1	52.2 ± 0.2	8.4 ± 0.2	9.3 ± 0.4	10.4 ± 0.5	11.4 ± 0.6	13.3 ± 0.7	14.7 ± 0.6	16.9 ± 0.5	0.016
12	$\text{hydroxymethylene (singlet)}$	hydroxymethylene (singlet)	26.1 ± 0.4	53.7 ± 0.2	8.7 ± 0.3	9.8 ± 0.6	11.1 ± 0.7	12.3 ± 0.8	14.3 ± 0.8	15.8 ± 0.7	17.8 ± 0.4	0.016
13	$\text{hydroxymethylene (triplet)}$	hydroxymethylene (triplet)	51.8 ± 0.9	58.3 ± 0.4	10.2 ± 0.3	11.2 ± 0.4	12.2 ± 0.4	12.9 ± 0.4	14.1 ± 0.4	15.0 ± 0.3	16.5 ± 0.3	0.022
14	methoxy	methoxy	4.9 ± 0.4	54.4 ± 0.3	9.9 ± 0.5	11.6 ± 0.7	13.3 ± 0.8	14.8 ± 0.8	17.2 ± 0.8	19.0 ± 0.8	21.9 ± 0.6	0.021
15	hydroxymethyl	hydroxymethyl	-3.6 ± 0.4	58.2 ± 0.5	11.4 ± 0.5	13.0 ± 0.6	14.3 ± 0.6	15.5 ± 0.6	17.2 ± 0.6	18.6 ± 0.6	20.9 ± 0.5	0.018
16	methanol	methanol	-48.2 ± 0.3	57.2 ± 0.4	10.6 ± 0.4	12.4 ± 0.7	14.3 ± 0.9	16.0 ± 1.0	19.0 ± 1.0	21.2 ± 1.0	25.0 ± 0.8	0.009
17	O_2	O_2	0.0 ± 0.0	48.9 ± 0.1	7.0 ± 0.0	7.2 ± 0.1	7.4 ± 0.1	7.6 ± 0.1	8.0 ± 0.1	8.2 ± 0.1	8.6 ± 0.1	0.007
18	HO_2	HO_2	2.7 ± 0.2	54.6 ± 0.2	8.3 ± 0.1	8.8 ± 0.2	9.4 ± 0.3	9.9 ± 0.3	10.7 ± 0.3	11.3 ± 0.3	12.3 ± 0.2	0.037
19	HOOH	HOOH	-32.1 ± 0.3	55.8 ± 0.3	9.9 ± 0.3	10.8 ± 0.4	11.7 ± 0.4	12.5 ± 0.4	13.7 ± 0.4	14.7 ± 0.4	16.3 ± 0.3	0.011
20	CO_2	CO_2	-94.1 ± 0.1	51.0 ± 0.3	8.9 ± 0.3	9.8 ± 0.3	10.6 ± 0.4	11.3 ± 0.3	12.2 ± 0.3	12.9 ± 0.3	13.8 ± 0.2	0.018
21		hydroxycarbonyl	-43.7 ± 0.5	60.2 ± 0.6	11.3 ± 0.6	12.8 ± 0.6	14.0 ± 0.5	14.8 ± 0.4	16.1 ± 0.3	16.9 ± 0.2	17.9 ± 0.1	0.024
22		formyloxy	-30.2 ± 0.5	60.3 ± 0.5	12.2 ± 0.4	13.4 ± 0.5	14.4 ± 0.5	15.2 ± 0.5	16.5 ± 0.5	17.3 ± 0.4	18.5 ± 0.2	0.022

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
23		formic acid	-90.5 ± 0.1	59.5 ± 0.5	11.0 ± 0.7	13.1 ± 0.9	15.1 ± 1.1	16.8 ± 1.1	19.4 ± 0.9	21.1 ± 0.7	23.3 ± 0.2	0.017
24		methylperoxy	3.3 ± 0.6	64.4 ± 0.5	12.1 ± 0.5	14.2 ± 0.8	16.2 ± 0.9	18.0 ± 1.0	20.9 ± 1.0	23.0 ± 0.9	26.3 ± 0.7	0.036
25		hydroxymethoxy	-40.6 ± 0.9	64.5 ± 0.7	13.2 ± 0.9	15.9 ± 1.0	18.2 ± 1.0	19.9 ± 0.9	22.4 ± 0.7	24.2 ± 0.7	26.8 ± 0.5	0.027
26		methylhydroperoxide	-30.7 ± 0.9	67.1 ± 0.8	14.6 ± 0.7	17.1 ± 0.9	19.4 ± 1.0	21.4 ± 1.0	24.5 ± 1.0	26.8 ± 0.9	30.5 ± 0.7	0.011
27		dioxirane	-39.1 ± 0.9	61.0 ± 0.5	11.6 ± 0.6	13.4 ± 0.6	14.7 ± 0.6	15.7 ± 0.5	17.0 ± 0.4	17.8 ± 0.3	18.8 ± 0.2	0.02
28		formylperoxy	-25.2 ± 0.9	66.2 ± 0.9	14.3 ± 0.9	16.5 ± 0.9	18.3 ± 0.8	19.6 ± 0.7	21.4 ± 0.5	22.5 ± 0.3	23.8 ± 0.1	0.031
29		performic acid	-69.1 ± 0.9	67.2 ± 1.2	17.2 ± 1.0	19.7 ± 0.7	21.3 ± 0.4	22.5 ± 0.4	24.1 ± 0.4	25.4 ± 0.4	27.5 ± 0.4	0.019
30		hydroperoxy-methoxy	-21.5 ± 0.9	72.6 ± 1.5	19.1 ± 0.9	21.8 ± 0.6	23.8 ± 0.5	25.3 ± 0.5	27.5 ± 0.5	29.2 ± 0.5	31.9 ± 0.5	0.020
31		hydroxymethylperoxy	-39.5 ± 0.9	72.5 ± 1.3	17.7 ± 0.8	20.4 ± 0.8	22.6 ± 0.8	24.3 ± 0.7	26.9 ± 0.6	28.7 ± 0.6	31.5 ± 0.5	0.031
32		hydroperoxy-methanol	-75.3 ± 0.9	72.8 ± 1.6	19.9 ± 1.0	23.2 ± 1.2	26.0 ± 1.1	28.1 ± 0.9	31.1 ± 0.7	33.1 ± 0.6	36.2 ± 0.4	0.013
33		C ₂ (singlet)	197.6 ± 0.9	45.5 ± 0.1	7.0 ± 0.0	7.1 ± 0.1	7.2 ± 0.1	7.4 ± 0.1	7.8 ± 0.1	8.1 ± 0.1	8.5 ± 0.1	0.041
34		C ₂ (triplet)	199.4 ± 0.9	47.8 ± 0.1	7.0 ± 0.0	7.1 ± 0.1	7.3 ± 0.1	7.6 ± 0.1	7.9 ± 0.1	8.2 ± 0.1	8.6 ± 0.1	0.020
35		ethynyl (HC ₂)	135.7 ± 0.1	51.6 ± 0.4	10.3 ± 0.1	10.6 ± 0.1	10.9 ± 0.1	11.2 ± 0.2	11.7 ± 0.2	12.2 ± 0.2	13.2 ± 0.2	0.017
36		acetylene	54.6 ± 0.1	47.7 ± 0.4	10.3 ± 0.5	11.8 ± 0.5	12.9 ± 0.5	13.7 ± 0.4	14.9 ± 0.5	16.0 ± 0.5	17.8 ± 0.4	0.013
37		acetylene (triplet)	143.7 ± 0.9	54.2 ± 0.3	9.6 ± 0.4	10.9 ± 0.5	12.0 ± 0.5	12.9 ± 0.5	14.3 ± 0.5	15.4 ± 0.5	17.2 ± 0.4	0.011
38		vinylidene (singlet)	98.4 ± 0.3	53.1 ± 0.4	10.5 ± 0.3	11.5 ± 0.4	12.4 ± 0.4	13.1 ± 0.4	14.4 ± 0.5	15.4 ± 0.5	17.2 ± 0.4	0.018
39		vinylidene (triplet)	145.9 ± 0.9	55.6 ± 0.3	9.3 ± 0.3	10.5 ± 0.5	11.5 ± 0.5	12.5 ± 0.5	14.0 ± 0.5	15.2 ± 0.5	17.1 ± 0.4	0.021
40		vinyl	71.2 ± 0.2	55.8 ± 0.4	10.4 ± 0.6	12.3 ± 0.7	13.9 ± 0.7	15.2 ± 0.7	17.4 ± 0.8	19.0 ± 0.7	21.8 ± 0.6	0.017
41		ethynylidyne	120.4 ± 0.9	56.5 ± 0.4	10.5 ± 0.5	12.2 ± 0.7	13.9 ± 0.8	15.3 ± 0.8	17.5 ± 0.8	19.3 ± 0.8	22.0 ± 0.6	0.015

Table 3. continued
























No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
42		ethene	12.5 ± 0.1	52.3 ± 0.4	10.2 ± 0.7	12.5 ± 0.9	14.7 ± 1.0	16.7 ± 1.1	19.8 ± 1.1	22.2 ± 1.1	26.1 ± 0.8	0.011
43		ethene (triplet)	79.1 ± 0.9	57.0 ± 0.6	13.2 ± 0.7	15.4 ± 0.8	17.2 ± 0.8	18.7 ± 0.9	21.2 ± 0.9	23.2 ± 0.9	26.5 ± 0.7	0.011
44		ethylidene (singlet)	87.5 ± 0.5	57.9 ± 0.4	11.5 ± 0.6	13.5 ± 0.8	15.4 ± 0.9	17.1 ± 1.0	20.0 ± 1.0	22.2 ± 1.0	25.8 ± 0.7	0.013
45		ethylidene (triplet)	84.8 ± 0.9	59.1 ± 0.4	11.0 ± 0.6	13.1 ± 0.8	15.1 ± 0.9	16.9 ± 1.0	19.7 ± 1.0	22.0 ± 1.0	25.6 ± 0.8	0.014
46		ethyl	28.9 ± 0.4	59.1 ± 0.5	12.3 ± 0.7	14.8 ± 1.0	17.2 ± 1.1	19.3 ± 1.2	22.8 ± 1.2	25.6 ± 1.2	30.1 ± 1.0	0.010
47		ethane	-20.0 ± 0.1	54.7 ± 0.6	12.6 ± 0.8	15.5 ± 1.1	18.4 ± 1.3	21.1 ± 1.4	25.5 ± 1.5	29.0 ± 1.5	34.6 ± 1.2	0.008
48		C ₂ O (singlet)	110.4 ± 0.9	53.6 ± 0.4	10.2 ± 0.3	11.0 ± 0.3	11.6 ± 0.3	12.2 ± 0.3	12.9 ± 0.3	13.5 ± 0.2	14.1 ± 0.1	0.023
49		C ₂ O (triplet)	91.0 ± 0.8	55.8 ± 0.4	10.3 ± 0.3	11.1 ± 0.3	11.7 ± 0.3	12.2 ± 0.3	13.0 ± 0.2	13.5 ± 0.2	14.2 ± 0.1	0.028
50		ketenyl	42.9 ± 0.5	58.8 ± 0.6	12.0 ± 0.4	13.1 ± 0.4	13.9 ± 0.4	14.6 ± 0.4	15.7 ± 0.4	16.6 ± 0.4	17.9 ± 0.3	0.026
51		ethynol	22.0 ± 0.5	59.1 ± 0.7	13.4 ± 0.6	15.2 ± 0.6	16.5 ± 0.6	17.5 ± 0.5	19.0 ± 0.5	20.2 ± 0.5	22.3 ± 0.5	0.013
52		ketene	-11.7 ± 0.1	57.6 ± 0.6	12.3 ± 0.6	14.1 ± 0.6	15.6 ± 0.7	16.8 ± 0.7	18.7 ± 0.7	20.1 ± 0.6	22.4 ± 0.5	0.017
53		CHCHO (triplet)	39.0 ± 0.9	62.8 ± 0.8	13.1 ± 0.8	15.2 ± 0.8	16.9 ± 0.7	18.2 ± 0.6	20.0 ± 0.4	21.1 ± 0.3	22.7 ± 0.2	0.028
54		oxirene	65.1 ± 0.9	60.5 ± 0.7	13.2 ± 0.6	15.1 ± 0.7	16.5 ± 0.6	17.7 ± 0.6	19.4 ± 0.6	20.6 ± 0.6	22.7 ± 0.4	0.014
55		oxiranyl	40.0 ± 0.9	60.4 ± 0.5	11.2 ± 0.9	14.2 ± 1.1	16.7 ± 1.1	18.8 ± 1.1	21.8 ± 1.0	24.0 ± 0.9	27.3 ± 0.7	0.022
56		2-hydroxyl-vinyl	31.5 ± 0.9	62.7 ± 0.9	14.7 ± 1.2	17.7 ± 1.2	20.0 ± 1.0	21.6 ± 0.7	23.6 ± 0.4	24.9 ± 0.3	27.0 ± 0.3	0.016
57		1-hydroxyl-vinyl	27.8 ± 0.9	64.1 ± 0.8	14.4 ± 0.9	16.9 ± 0.8	18.7 ± 0.8	20.2 ± 0.7	22.3 ± 0.6	23.9 ± 0.6	26.5 ± 0.5	0.019
58		vinoxy	4.4 ± 0.9	61.9 ± 0.6	12.7 ± 0.8	15.3 ± 1.0	17.5 ± 1.0	19.3 ± 1.0	22.1 ± 1.0	24.2 ± 0.9	27.4 ± 0.7	0.023
59		acetyl	-2.3 ± 0.1	63.7 ± 0.5	12.1 ± 0.6	14.1 ± 0.8	16.1 ± 0.9	17.8 ± 1.0	20.7 ± 1.0	22.8 ± 0.9	26.2 ± 0.7	0.022
60		oxirane	-12.4 ± 0.6	57.9 ± 0.5	11.4 ± 1.0	14.9 ± 1.3	18.0 ± 1.4	20.6 ± 1.4	24.5 ± 1.3	27.4 ± 1.2	31.7 ± 0.9	0.011
61		ethanol	-29.9 ± 0.9	62.2 ± 1.0	15.0 ± 1.0	18.1 ± 1.0	20.5 ± 1.0	22.5 ± 0.9	25.4 ± 0.8	27.6 ± 0.8	31.1 ± 0.7	0.013
62		acetaldehyde	-39.6 ± 0.1	63.0 ± 0.6	13.0 ± 0.6	15.5 ± 1.0	18.0 ± 1.1	20.2 ± 1.2	23.8 ± 1.2	26.6 ± 1.2	30.9 ± 0.9	0.015
63		ethoxy	-3.1 ± 0.4	66.8 ± 1.0	15.8 ± 0.8	18.8 ± 1.1	21.7 ± 1.2	24.1 ± 1.3	28.2 ± 1.3	31.2 ± 1.3	36.0 ± 1.0	0.020
64		methoxy-methyl	0.8 ± 0.9	67.3 ± 0.9	15.5 ± 0.7	18.3 ± 1.1	21.0 ± 1.2	23.5 ± 1.3	27.4 ± 1.3	30.4 ± 1.2	35.1 ± 0.9	0.017

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
65		2-hydroxyethyl	-5.9 ± 0.4	69.4 ± 1.1	16.8 ± 0.5	19.5 ± 0.8	22.0 ± 1.0	24.1 ± 1.1	27.6 ± 1.1	30.3 ± 1.1	34.8 ± 0.9	0.012
66		1-hydroxyethyl	-13.0 ± 0.3	68.1 ± 0.9	15.8 ± 0.8	18.8 ± 1.0	21.5 ± 1.2	23.8 ± 1.2	27.6 ± 1.2	30.4 ± 1.1	34.9 ± 0.9	0.015
67		ethanol	-56.4 ± 0.4	66.8 ± 0.9	15.7 ± 1.0	19.2 ± 1.3	22.6 ± 1.4	25.5 ± 1.5	30.1 ± 1.5	33.6 ± 1.4	39.3 ± 1.2	0.009
68		dimethyl-ether	-43.9 ± 0.2	63.9 ± 1.0	15.8 ± 0.8	18.9 ± 1.1	22.1 ± 1.3	24.9 ± 1.4	29.8 ± 1.5	33.5 ± 1.5	39.4 ± 1.2	0.010
69		formyl (triplet)	4.8 ± 0.9	61.2 ± 0.8	14.2 ± 0.4	15.2 ± 0.3	16.0 ± 0.4	16.6 ± 0.4	17.7 ± 0.4	18.5 ± 0.3	19.6 ± 0.2	0.026
70		glyoxalyl	-14.9 ± 0.4	67.2 ± 0.7	13.9 ± 0.6	15.6 ± 0.7	17.1 ± 0.7	18.3 ± 0.7	20.2 ± 0.6	21.6 ± 0.6	23.5 ± 0.4	0.020
71		1-hydroxyethyl-ketenyl	5.3 ± 0.9	65.7 ± 0.8	14.3 ± 0.6	16.1 ± 0.6	17.5 ± 0.6	18.6 ± 0.6	20.3 ± 0.6	21.5 ± 0.5	23.2 ± 0.4	0.020
72		glyoxal	-50.9 ± 0.9	64.6 ± 0.8	14.5 ± 0.8	17.0 ± 1.1	19.4 ± 1.2	21.4 ± 1.1	24.3 ± 0.8	26.0 ± 0.5	28.2 ± 0.2	0.016
73		oxiranone (acetone)	-41.0 ± 0.9	63.1 ± 0.7	13.1 ± 0.9	16.0 ± 1.1	18.4 ± 1.1	20.4 ± 1.0	23.2 ± 0.9	25.2 ± 0.8	28.0 ± 0.6	0.017
74		hydroxyketene	-36.2 ± 0.9	66.6 ± 1.0	15.9 ± 0.7	18.2 ± 0.7	19.9 ± 0.7	21.2 ± 0.6	23.3 ± 0.6	24.8 ± 0.6	27.1 ± 0.5	0.016
75		ethynediol	-5.1 ± 0.9	67.4 ± 1.1	17.3 ± 0.5	19.0 ± 0.5	20.3 ± 0.5	21.5 ± 0.5	23.2 ± 0.6	24.5 ± 0.6	26.8 ± 0.5	0.013
76		vinylperoxy	27.5 ± 0.9	68.0 ± 1.1	16.8 ± 1.1	20.1 ± 1.1	22.7 ± 1.1	24.8 ± 1.0	27.7 ± 0.8	29.7 ± 0.7	32.6 ± 0.5	0.035
77		2-hydroperoxyvinyl	53.5 ± 0.9	74.8 ± 1.2	18.5 ± 0.6	21.0 ± 0.8	23.1 ± 0.8	24.7 ± 0.8	27.1 ± 0.7	28.8 ± 0.6	31.5 ± 0.5	0.016
78		formyl-methoxy	-18.3 ± 0.9	70.1 ± 0.9	15.7 ± 1.1	19.0 ± 1.3	21.8 ± 1.3	24.0 ± 1.2	27.2 ± 1.0	29.4 ± 0.8	32.6 ± 0.6	0.029
79		formyl-methoxy	-37.3 ± 0.9	70.1 ± 1.1	17.2 ± 1.0	20.2 ± 1.3	22.9 ± 1.4	25.1 ± 1.3	28.4 ± 1.0	30.6 ± 0.8	33.3 ± 0.3	0.019
80		methoxy-formyl	-37.6 ± 0.9	70.5 ± 0.8	15.3 ± 0.7	17.7 ± 1.0	20.2 ± 1.2	22.4 ± 1.2	25.8 ± 1.2	28.3 ± 1.0	31.8 ± 0.6	0.023
81		oxiranyloxy	-8.9 ± 0.9	67.8 ± 0.9	15.5 ± 1.1	18.9 ± 1.3	21.7 ± 1.3	24.0 ± 1.2	27.3 ± 1.1	29.6 ± 1.0	33.1 ± 0.7	0.035

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
82		acetyloxy	-44.9 ± 0.9	67.7 ± 0.7	14.6 ± 0.9	17.7 ± 1.2	20.3 ± 1.2	22.6 ± 1.2	25.9 ± 1.1	28.3 ± 1.0	31.9 ± 0.7	0.021
83		2-hydroxyl-vinoyloxy	-55.8 ± 0.9	67.8 ± 1.0	16.5 ± 1.1	19.9 ± 1.3	22.7 ± 1.4	25.0 ± 1.4	28.5 ± 1.3	30.8 ± 1.0	33.8 ± 0.3	0.018
84		vinyl-hydroperoxide	-9.2 ± 0.9	73.0 ± 1.2	18.4 ± 0.8	21.6 ± 1.1	24.4 ± 1.2	26.7 ± 1.2	30.1 ± 1.0	32.5 ± 0.9	36.2 ± 0.7	0.014
85		acetic acid	-103.3 ± 0.4	68.2 ± 0.8	15.5 ± 1.2	19.2 ± 1.5	22.5 ± 1.6	25.3 ± 1.7	29.8 ± 1.6	33.0 ± 1.4	37.4 ± 0.7	0.015
86		methyl formate	-85.6 ± 0.2	69.0 ± 0.9	15.5 ± 0.9	18.7 ± 1.4	22.0 ± 1.7	24.9 ± 1.8	29.6 ± 1.6	32.9 ± 1.4	37.4 ± 0.7	0.016
87		cis-ethendiol	-68.8 ± 0.9	68.8 ± 1.1	17.1 ± 1.5	21.4 ± 1.9	25.1 ± 1.8	27.9 ± 1.5	31.4 ± 0.9	33.6 ± 0.6	36.6 ± 0.4	0.013
88		hydroxyl-acetaldehyde	-76.0 ± 0.9	68.7 ± 1.2	17.7 ± 1.6	22.0 ± 1.9	25.6 ± 1.7	28.4 ± 1.3	32.0 ± 0.8	34.1 ± 0.5	37.2 ± 0.3	0.014
89		ethylperoxy	-5.0 ± 0.9	74.2 ± 1.1	17.6 ± 1.1	21.3 ± 1.4	24.7 ± 1.4	27.6 ± 1.4	32.1 ± 1.4	35.4 ± 1.3	40.5 ± 1.0	0.032
90		hydroperoxyl-ethyl	12.2 ± 0.9	79.0 ± 1.3	19.8 ± 1.0	23.3 ± 1.2	26.4 ± 1.3	28.9 ± 1.3	32.8 ± 1.2	35.6 ± 1.1	40.1 ± 0.9	0.013
91		1,2-dihydroxyl-ethyl	-50.0 ± 0.9	75.2 ± 1.8	21.8 ± 1.3	25.8 ± 1.3	29.0 ± 1.1	31.4 ± 0.9	34.7 ± 0.7	36.9 ± 0.6	40.6 ± 0.6	0.016
92		3-hydroxyl-ethoxy	-39.3 ± 0.9	71.4 ± 1.8	20.9 ± 2.0	25.8 ± 1.5	29.1 ± 1.0	31.4 ± 0.7	34.6 ± 0.6	37.1 ± 0.7	41.2 ± 0.7	0.019
93		hydroxyl-methoxy	-43.8 ± 0.9	73.6 ± 1.7	20.9 ± 1.3	24.7 ± 1.1	27.5 ± 0.9	29.7 ± 0.7	33.1 ± 0.8	35.6 ± 0.8	39.9 ± 0.8	0.016
94		methoxymethoxy	-42.7 ± 0.9	74.4 ± 2.0	22.8 ± 1.1	26.0 ± 0.7	28.5 ± 0.6	30.4 ± 0.6	33.6 ± 0.7	36.0 ± 0.8	40.1 ± 0.7	0.016
95		methoxymethyl-methoxy	-35.2 ± 0.9	74.2 ± 1.1	17.4 ± 1.0	21.2 ± 1.4	24.7 ± 1.5	27.6 ± 1.5	32.3 ± 1.5	35.6 ± 1.4	40.8 ± 1.0	0.022

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
96		ethyl- hydroperoxide	-38.5 ± 0.9	75.2 ± 1.4	20.0 ± 1.2	24.1 ± 1.5	27.8 ± 1.5	30.8 ± 1.5	35.6 ± 1.5	39.2 ± 1.4	44.8 ± 1.0	0.012
97		dimethyl-peroxide	-29.1 ± 0.9	72.2 ± 1.3	19.5 ± 1.1	23.3 ± 1.4	26.9 ± 1.5	30.0 ± 1.6	35.0 ± 1.6	38.9 ± 1.5	44.8 ± 1.2	0.012
98		ketenylperoxy	19.2 ± 0.9	75.8 ± 1.3	18.7 ± 0.6	20.7 ± 0.6	22.4 ± 0.6	23.6 ± 0.5	25.4 ± 0.5	26.6 ± 0.4	28.4 ± 0.3	0.043
99		acetylperoxy	-37.5 ± 0.9	76.2 ± 1.4	19.9 ± 0.8	23.1 ± 1.1	25.8 ± 1.2	28.1 ± 1.1	31.6 ± 1.0	33.9 ± 0.9	37.3 ± 0.6	0.029
100		formylmethylperoxy	-18.9 ± 0.9	77.6 ± 1.4	19.8 ± 1.0	23.2 ± 1.2	26.1 ± 1.1	28.4 ± 1.0	31.7 ± 0.9	34.0 ± 0.8	37.3 ± 0.6	0.031
101		hydroperoxyl- acetyl	-17.8 ± 0.9	79.3 ± 1.8	22.3 ± 1.2	25.8 ± 1.2	28.5 ± 0.9	30.4 ± 0.7	33.1 ± 0.5	34.8 ± 0.4	37.4 ± 0.3	0.020
102		hydroperoxyl- vinoxy	-35.2 ± 0.9	73.7 ± 1.6	21.0 ± 1.6	25.4 ± 1.9	29.0 ± 1.8	31.7 ± 1.5	35.2 ± 1.0	37.3 ± 0.6	39.6 ± -0.0	0.021
103		methylperoxy- methoxy	-29.3 ± 0.9	81.3 ± 1.8	22.7 ± 1.2	27.0 ± 1.3	30.5 ± 1.4	33.5 ± 1.4	38.0 ± 1.3	41.4 ± 1.3	46.4 ± 0.9	0.019
104		2-hydroperoxyl- ethylperoxy ^a	-21.5 ± 0.9	89.7 ± 2.8	29.6 ± 1.2	33.8 ± 0.9	37.0 ± 0.8	39.6 ± 0.8	43.5 ± 0.9	46.5 ± 1.0	51.2 ± 0.8	0.028
105		H2CCC (singlet)	132.1 ± 0.9	58.7 ± 0.6	12.4 ± 0.5	14.0 ± 0.6	15.4 ± 0.7	16.6 ± 0.7	18.6 ± 0.7	20.1 ± 0.7	22.5 ± 0.5	0.019
106		HCCCH (singlet)	142.7 ± 0.9	59.5 ± 0.8	14.1 ± 0.5	15.7 ± 0.6	17.0 ± 0.6	18.0 ± 0.6	19.6 ± 0.6	20.9 ± 0.5	22.9 ± 0.4	0.031
107		HCCCH (triplet)	130.5 ± 0.9	63.8 ± 1.0	16.8 ± 0.3	17.7 ± 0.3	18.5 ± 0.4	19.1 ± 0.4	20.3 ± 0.4	21.2 ± 0.4	22.9 ± 0.4	0.013
108		propargyl	84.2 ± 0.3	60.6 ± 0.8	14.9 ± 0.8	17.2 ± 0.8	19.0 ± 0.8	20.4 ± 0.8	22.7 ± 0.8	24.4 ± 0.8	27.3 ± 0.6	0.023
109		allene	45.1 ± 0.5	59.3 ± 0.8	14.0 ± 1.0	17.0 ± 1.1	19.6 ± 1.2	21.8 ± 1.2	25.2 ± 1.2	27.7 ± 1.1	31.8 ± 0.9	0.013
110		propyne	44.3 ± 0.2	59.0 ± 0.8	14.4 ± 0.9	17.1 ± 1.0	19.5 ± 1.1	21.6 ± 1.1	24.9 ± 1.2	27.5 ± 1.1	31.6 ± 0.9	0.012
111		cyclopropene	67.6 ± 0.4	58.0 ± 0.6	12.5 ± 1.1	16.0 ± 1.3	19.0 ± 1.3	21.4 ± 1.3	25.1 ± 1.2	27.7 ± 1.1	31.8 ± 0.9	0.010

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
112		allyl	40.6 ± 0.9	61.5 ± 0.8	14.9 ± 1.2	18.7 ± 1.4	22.0 ± 1.5	24.6 ± 1.5	28.7 ± 1.4	31.8 ± 1.3	36.6 ± 1.0	0.011
113		cyclopropyl	69.9 ± 0.9	61.6 ± 0.7	13.6 ± 1.3	17.8 ± 1.6	21.4 ± 1.6	24.3 ± 1.6	28.6 ± 1.5	31.8 ± 1.4	36.7 ± 1.0	0.012
114		1-methyl-vinyl	60.5 ± 0.9	65.4 ± 0.8	15.1 ± 0.8	18.2 ± 1.1	21.0 ± 1.3	23.6 ± 1.4	27.7 ± 1.4	30.8 ± 1.3	35.7 ± 1.0	0.015
115		2-methyl-vinyl	64.1 ± 0.9	64.9 ± 0.9	15.3 ± 0.9	18.5 ± 1.1	21.4 ± 1.3	23.8 ± 1.3	27.8 ± 1.3	30.9 ± 1.3	35.7 ± 1.0	0.015
116		cyclopropane	13.0 ± 0.4	56.7 ± 0.7	13.4 ± 1.4	18.1 ± 1.8	22.3 ± 1.9	25.8 ± 1.9	31.1 ± 1.8	35.0 ± 1.7	41.0 ± 1.3	0.008
117		propene (singlet)	4.6 ± 0.3	63.6 ± 0.9	15.4 ± 1.0	19.1 ± 1.4	22.6 ± 1.5	25.6 ± 1.6	30.5 ± 1.7	34.2 ± 1.6	40.2 ± 1.2	0.010
118		propene (triplet)	71.6 ± 0.9	70.5 ± 0.9	17.3 ± 1.1	20.9 ± 1.4	24.1 ± 1.5	26.9 ± 1.6	31.5 ± 1.6	34.9 ± 1.5	40.5 ± 1.1	0.012
119		n-propyl	24.3 ± 0.9	69.3 ± 1.0	17.3 ± 1.2	21.5 ± 1.5	25.3 ± 1.7	28.5 ± 1.7	33.8 ± 1.7	37.8 ± 1.7	44.3 ± 1.3	0.010
120		iso-propyl	21.2 ± 0.9	68.9 ± 0.8	16.4 ± 1.0	20.3 ± 1.5	24.1 ± 1.8	27.5 ± 1.9	33.1 ± 1.9	37.3 ± 1.9	44.1 ± 1.4	0.011
121		propane	-25.2 ± 0.3	66.1 ± 1.2	17.8 ± 1.4	22.4 ± 1.7	26.7 ± 1.8	30.5 ± 1.9	36.6 ± 2.0	41.3 ± 1.9	48.9 ± 1.5	0.008
122		HCCCO	69.1 ± 0.9	66.4 ± 0.9	15.6 ± 0.5	17.1 ± 0.5	18.2 ± 0.5	19.2 ± 0.5	20.6 ± 0.5	21.7 ± 0.5	23.4 ± 0.4	0.025
123		propynal	31.8 ± 0.9	65.5 ± 0.9	15.1 ± 0.8	17.5 ± 0.9	19.4 ± 0.9	21.0 ± 0.9	23.4 ± 0.8	25.2 ± 0.8	28.0 ± 0.6	0.016
124		propadienal	31.2 ± 0.9	66.1 ± 0.9	15.1 ± 0.7	17.3 ± 0.8	19.1 ± 0.9	20.7 ± 0.9	23.2 ± 0.9	25.1 ± 0.8	27.9 ± 0.6	0.019
125		vinyl-formyl	23.2 ± 0.9	67.9 ± 0.9	15.6 ± 0.9	18.6 ± 1.1	21.2 ± 1.2	23.3 ± 1.2	26.6 ± 1.1	29.1 ± 1.0	32.7 ± 0.8	0.022
126		1-formyl-vinyl	45.2 ± 0.9	70.3 ± 1.0	16.3 ± 0.9	19.1 ± 1.1	21.6 ± 1.2	23.7 ± 1.2	27.0 ± 1.1	29.4 ± 1.0	33.0 ± 0.7	0.019
127		2-formyl-vinyl	44.4 ± 0.9	67.3 ± 1.0	16.2 ± 1.2	19.7 ± 1.5	22.7 ± 1.4	25.0 ± 1.3	28.3 ± 0.9	30.4 ± 0.7	33.2 ± 0.4	0.019
128		acrolein (singlet)	-15.5 ± 0.9	65.3 ± 1.1	16.9 ± 1.1	20.4 ± 1.3	23.5 ± 1.4	26.1 ± 1.4	30.1 ± 1.3	33.0 ± 1.1	37.3 ± 0.8	0.015
129		acrolein (triplet)	45.8 ± 0.9	69.7 ± 1.3	18.8 ± 1.0	22.2 ± 1.2	25.1 ± 1.3	27.5 ± 1.3	31.2 ± 1.3	33.9 ± 1.2	38.0 ± 0.8	0.021
130		methyl-ketene	-15.1 ± 0.9	68.6 ± 1.0	16.5 ± 0.9	19.5 ± 1.1	22.4 ± 1.3	24.8 ± 1.3	28.8 ± 1.3	31.7 ± 1.3	36.3 ± 1.0	0.016
131		oxetene	12.6 ± 0.9	62.9 ± 0.8	14.1 ± 1.3	18.4 ± 1.7	22.2 ± 1.7	25.2 ± 1.6	29.6 ± 1.5	32.7 ± 1.3	37.4 ± 0.9	0.015
132		allyloxy	23.7 ± 0.9	72.6 ± 1.3	18.5 ± 1.1	22.4 ± 1.4	25.8 ± 1.5	28.8 ± 1.5	33.3 ± 1.5	36.6 ± 1.4	41.6 ± 1.0	0.020

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
133		propen-2-oxo	-6.9 ± 0.9	72.9 ± 1.0	17.9 ± 1.3	21.8 ± 1.5	25.3 ± 1.6	28.3 ± 1.6	32.8 ± 1.6	36.2 ± 1.4	41.2 ± 1.0	0.019
134		2-formyl-ethyl	6.6 ± 0.9	75.4 ± 1.3	19.4 ± 0.6	22.5 ± 1.0	25.4 ± 1.2	28.1 ± 1.3	32.3 ± 1.4	35.5 ± 1.3	40.6 ± 1.0	0.015
135		oxiranyl-methyl	26.0 ± 0.9	69.9 ± 1.2	17.9 ± 1.4	22.4 ± 1.7	26.2 ± 1.7	29.2 ± 1.6	33.6 ± 1.4	36.8 ± 1.3	41.7 ± 1.0	0.015
136		vinoxyl-methyl	22.1 ± 0.9	72.9 ± 1.2	19.1 ± 1.3	23.1 ± 1.5	26.5 ± 1.5	29.2 ± 1.4	33.4 ± 1.3	36.4 ± 1.2	41.0 ± 0.9	0.018
137		1-formyl-ethyl	-5.7 ± 0.9	71.3 ± 1.2	18.1 ± 0.9	21.6 ± 1.3	24.9 ± 1.5	27.9 ± 1.6	32.5 ± 1.6	36.0 ± 1.5	41.4 ± 1.1	0.020
138		propionyl	-6.9 ± 0.9	74.7 ± 1.1	17.8 ± 0.7	20.9 ± 1.1	24.0 ± 1.3	26.8 ± 1.4	31.4 ± 1.5	34.8 ± 1.4	40.2 ± 1.1	0.019
139		2-oxetanyl	24.4 ± 0.9	67.6 ± 0.9	15.3 ± 1.4	20.1 ± 1.8	24.3 ± 1.9	27.8 ± 1.9	33.0 ± 1.7	36.7 ± 1.6	42.2 ± 1.1	0.018
140		3-oxetanyl	30.6 ± 0.9	66.8 ± 1.0	16.2 ± 1.4	20.8 ± 1.8	24.9 ± 1.9	28.3 ± 1.8	33.4 ± 1.7	37.0 ± 1.5	42.4 ± 1.1	0.013
141		1-hydroxyl-allyl	-2.2 ± 0.9	70.2 ± 1.4	19.3 ± 1.3	23.6 ± 1.5	27.1 ± 1.5	29.8 ± 1.4	33.9 ± 1.3	36.9 ± 1.2	41.6 ± 0.9	0.014
142		2-hydroxyl-allyl	-1.6 ± 0.9	69.3 ± 1.4	19.7 ± 1.5	24.2 ± 1.5	27.7 ± 1.4	30.3 ± 1.3	34.2 ± 1.2	37.0 ± 1.1	41.5 ± 0.9	0.024
143		acetone	-52.0 ± 0.4	70.9 ± 0.9	17.5 ± 1.2	21.7 ± 1.6	25.5 ± 1.8	28.9 ± 1.9	34.3 ± 1.9	38.4 ± 1.8	44.8 ± 1.3	0.014
144		propanal	-45.0 ± 0.9	73.5 ± 1.3	18.9 ± 0.6	22.4 ± 1.2	26.0 ± 1.5	29.2 ± 1.7	34.6 ± 1.8	38.6 ± 1.7	44.9 ± 1.3	0.014
145		propen-1-ol	-35.8 ± 0.9	70.8 ± 1.6	20.7 ± 1.1	24.6 ± 1.2	28.0 ± 1.3	31.0 ± 1.4	35.7 ± 1.4	39.3 ± 1.4	45.0 ± 1.2	0.012
146		propen-2-ol	-40.6 ± 0.9	69.6 ± 1.6	20.6 ± 1.6	25.3 ± 1.6	29.1 ± 1.5	32.0 ± 1.4	36.5 ± 1.3	39.9 ± 1.3	45.3 ± 1.0	0.012
147		propylene oxide	-22.3 ± 0.9	68.5 ± 1.1	17.4 ± 1.4	22.1 ± 1.7	26.3 ± 1.9	29.9 ± 1.9	35.5 ± 1.8	39.6 ± 1.7	45.9 ± 1.3	0.011
148		oxetane	-19.0 ± 0.9	65.6 ± 0.9	15.2 ± 1.5	20.4 ± 2.1	25.2 ± 2.2	29.3 ± 2.2	35.5 ± 2.1	39.9 ± 1.9	46.6 ± 1.4	0.010
149		allyl-alcohol	-30.1 ± 0.9	72.6 ± 1.8	21.5 ± 0.7	25.0 ± 0.9	28.2 ± 1.1	31.0 ± 1.2	35.6 ± 1.4	39.1 ± 1.4	44.9 ± 1.2	0.011

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
150		cyclopropanol	-24.2 ± 0.9	68.0 ± 1.2	18.0 ± 1.6	23.1 ± 1.8	27.4 ± 1.8	30.9 ± 1.8	36.1 ± 1.7	39.8 ± 1.6	45.8 ± 1.2	0.010
151		n-propoxy	-8.1 ± 0.9	75.7 ± 1.5	20.8 ± 1.4	25.5 ± 1.7	29.7 ± 1.8	33.3 ± 1.8	39.1 ± 1.8	43.4 ± 1.7	50.2 ± 1.3	0.018
152		iso-propoxy	-10.7 ± 0.9	72.5 ± 1.5	20.8 ± 1.4	25.6 ± 1.6	29.7 ± 1.7	33.3 ± 1.8	39.0 ± 1.8	43.2 ± 1.7	50.0 ± 1.4	0.018
153		3-hydroxyl-propyl	-11.5 ± 0.9	79.5 ± 1.6	22.0 ± 0.9	26.2 ± 1.4	30.1 ± 1.6	33.4 ± 1.6	38.7 ± 1.6	42.7 ± 1.6	49.1 ± 1.3	0.011
154		1-hydroxyl-propyl	-17.6 ± 0.9	78.7 ± 1.5	21.2 ± 1.2	25.7 ± 1.6	29.7 ± 1.7	33.1 ± 1.7	38.5 ± 1.7	42.6 ± 1.6	49.1 ± 1.3	0.014
155		1-methyl-2-hydroxyl-ethyl	-13.8 ± 0.9	80.4 ± 1.4	21.0 ± 0.9	25.1 ± 1.4	29.0 ± 1.6	32.4 ± 1.7	37.9 ± 1.8	42.1 ± 1.7	48.8 ± 1.4	0.012
156		2-hydroxyl-propyl	-14.7 ± 0.9	77.9 ± 1.7	22.7 ± 1.1	27.0 ± 1.4	30.7 ± 1.5	33.9 ± 1.5	38.9 ± 1.6	42.8 ± 1.5	49.1 ± 1.3	0.011
157		1-methyl-1-hydroxyl-ethyl	-22.9 ± 0.9	74.6 ± 1.6	21.8 ± 1.2	26.1 ± 1.5	29.9 ± 1.6	33.3 ± 1.6	38.6 ± 1.6	42.7 ± 1.6	49.1 ± 1.3	0.014
158		ethoxyl-methyl	-7.3 ± 0.9	76.1 ± 1.6	21.4 ± 1.1	25.7 ± 1.5	29.7 ± 1.7	33.2 ± 1.8	38.8 ± 1.7	42.9 ± 1.6	49.5 ± 1.2	0.016
159		2-methoxyl-ethyl	-1.3 ± 0.9	77.6 ± 1.5	21.2 ± 1.0	25.3 ± 1.4	29.2 ± 1.6	32.7 ± 1.7	38.3 ± 1.8	42.5 ± 1.7	49.2 ± 1.3	0.011
160		1-methoxyl-ethyl	-8.6 ± 0.9	75.5 ± 1.6	21.5 ± 1.2	25.8 ± 1.5	29.7 ± 1.6	33.1 ± 1.6	38.5 ± 1.6	42.6 ± 1.6	49.2 ± 1.3	0.016
161		n-propanol	-61.3 ± 0.9	76.3 ± 1.5	20.9 ± 1.4	25.9 ± 1.8	30.6 ± 2.0	34.6 ± 2.0	41.0 ± 2.0	45.9 ± 1.9	53.5 ± 1.5	0.009
162		iso-propanol	-65.4 ± 0.3	74.2 ± 1.6	21.8 ± 1.5	26.9 ± 1.8	31.5 ± 1.9	35.4 ± 1.9	41.5 ± 1.9	46.1 ± 1.9	53.6 ± 1.5	0.010
163		ethyl-methyl-ether	-51.9 ± 0.9	73.5 ± 1.9	22.6 ± 1.2	26.9 ± 1.4	31.1 ± 1.6	34.9 ± 1.8	41.2 ± 1.9	46.1 ± 1.9	53.8 ± 1.5	0.010
164		allylperoxy	21.2 ± 0.9	80.6 ± 1.5	21.1 ± 1.2	25.4 ± 1.4	29.2 ± 1.5	32.3 ± 1.6	37.2 ± 1.5	40.7 ± 1.4	46.1 ± 1.1	0.030
165		propen-1-peroxy	19.2 ± 0.9	76.7 ± 1.7	22.4 ± 1.3	26.8 ± 1.5	30.5 ± 1.5	33.6 ± 1.5	38.2 ± 1.4	41.6 ± 1.2	46.6 ± 0.9	0.033

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
166		propen-2-peroxy	16.0 ± 0.9	76.2 ± 1.8	23.1 ± 1.5	27.6 ± 1.5	31.3 ± 1.4	34.3 ± 1.3	38.6 ± 1.2	41.8 ± 1.1	46.6 ± 0.9	0.033
167		2-formyl-ethoxy	-25.7 ± 0.9	82.3 ± 1.4	20.7 ± 1.1	24.9 ± 1.5	28.8 ± 1.7	32.2 ± 1.7	37.3 ± 1.6	41.0 ± 1.5	46.5 ± 1.1	0.019
168		1-formyl-ethoxy	-27.2 ± 0.9	79.5 ± 1.6	22.1 ± 1.2	26.4 ± 1.5	30.2 ± 1.6	33.3 ± 1.6	38.1 ± 1.4	41.5 ± 1.3	46.6 ± 1.0	0.026
169		acetyl-methoxy	-31.3 ± 0.9	78.3 ± 1.4	21.1 ± 1.5	25.8 ± 1.9	29.9 ± 1.9	33.3 ± 1.8	38.3 ± 1.5	41.8 ± 1.3	46.8 ± 0.9	0.033
170		oxiranyl-methoxy	-2.7 ± 0.9	76.9 ± 1.4	19.8 ± 1.4	24.7 ± 1.8	29.1 ± 1.9	32.7 ± 1.9	38.0 ± 1.7	41.8 ± 1.5	47.3 ± 1.1	0.018
171		allyl-hydroperoxide	-11.9 ± 0.9	82.0 ± 2.1	25.1 ± 0.7	29.0 ± 1.1	32.7 ± 1.4	35.8 ± 1.4	40.8 ± 1.5	44.5 ± 1.4	50.2 ± 1.1	0.012
172		propen-1-hydroperoxide	-15.3 ± 0.9	81.6 ± 1.7	23.6 ± 1.3	28.0 ± 1.6	32.0 ± 1.7	35.3 ± 1.7	40.4 ± 1.6	44.2 ± 1.5	50.1 ± 1.2	0.013
173		propen-2-hydroperoxide	-19.8 ± 0.9	78.9 ± 2.0	24.9 ± 1.6	29.7 ± 1.5	33.5 ± 1.4	36.5 ± 1.3	41.1 ± 1.3	44.6 ± 1.3	50.2 ± 1.1	0.013
174		n-propylperoxy	-9.8 ± 0.9	83.5 ± 1.7	23.0 ± 1.5	28.2 ± 1.8	32.9 ± 2.0	36.9 ± 2.0	43.1 ± 1.9	47.7 ± 1.8	54.7 ± 1.4	0.014
175		iso-propylperoxy	-14.4 ± 0.9	80.9 ± 1.9	24.2 ± 1.4	29.2 ± 1.7	33.7 ± 1.8	37.4 ± 1.8	43.3 ± 1.8	47.8 ± 1.7	54.7 ± 1.4	0.014
176		3-hydroperoxyl-propyl	6.8 ± 0.9	88.5 ± 1.9	25.2 ± 1.6	30.4 ± 1.8	34.8 ± 1.8	38.4 ± 1.8	44.0 ± 1.7	48.1 ± 1.6	54.5 ± 1.2	0.014
177		3-hydroperoxyl-2-propyl	4.6 ± 0.9	88.2 ± 1.7	24.2 ± 1.3	29.1 ± 1.8	33.5 ± 1.9	37.3 ± 1.9	43.1 ± 1.9	47.4 ± 1.8	54.1 ± 1.3	0.013

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
178		2-hydroperoxyl-propyl	4.1 ± 0.9	86.9 ± 2.0	26.5 ± 1.3	31.3 ± 1.6	35.4 ± 1.7	38.9 ± 1.7	44.2 ± 1.6	48.2 ± 1.5	54.4 ± 1.2	0.029
179		n-propyl hydroperoxide	-43.3 ± 0.9	84.2 ± 2.0	25.7 ± 1.6	31.2 ± 1.9	36.1 ± 2.0	40.2 ± 2.0	46.7 ± 2.0	51.5 ± 1.9	59.0 ± 1.4	0.029
180		iso-propyl hydroperoxide	-47.7 ± 0.9	82.4 ± 2.1	26.9 ± 1.6	32.3 ± 1.9	37.1 ± 1.9	41.1 ± 1.9	47.3 ± 1.9	51.9 ± 1.8	59.2 ± 1.4	0.012
181		1-formyl ethylperoxy ^a	-28.7 ± 0.9	86.8 ± 2.0	25.6 ± 1.5	30.4 ± 1.7	34.5 ± 1.6	37.8 ± 1.5	42.7 ± 1.4	46.2 ± 1.2	51.4 ± 0.9	0.013
182		2-formyl ethylperoxy ^a	-27.5 ± 0.9	88.3 ± 2.4	27.2 ± 1.0	31.1 ± 0.9	34.5 ± 1.0	37.4 ± 1.2	42.2 ± 1.3	45.7 ± 1.3	51.2 ± 1.0	0.013
183		acetyl methylperoxy ^a	-32.0 ± 0.9	86.9 ± 2.0	25.2 ± 1.3	30.0 ± 1.6	34.0 ± 1.6	37.3 ± 1.6	42.3 ± 1.5	45.9 ± 1.3	51.3 ± 1.0	0.011
184		oxiranyl methylperoxy ^a	-3.8 ± 0.9	85.3 ± 1.8	23.6 ± 1.2	28.6 ± 1.7	33.1 ± 1.8	36.8 ± 1.8	42.3 ± 1.7	46.2 ± 1.5	51.9 ± 1.1	0.011
185		1-formyl-ethyl hydroperoxide	-64.0 ± 0.9	86.9 ± 2.4	28.7 ± 1.6	33.8 ± 1.7	38.1 ± 1.7	41.6 ± 1.6	46.8 ± 1.4	50.5 ± 1.2	56.0 ± 0.9	0.014
186		2-formyl-ethyl hydroperoxide	-61.7 ± 0.9	89.7 ± 2.7	29.4 ± 0.7	33.3 ± 1.0	37.0 ± 1.3	40.2 ± 1.4	45.5 ± 1.5	49.4 ± 1.4	55.5 ± 1.1	0.014





Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
187		acetyl-methyl-hydroperoxide	-69.0 ± 0.9	85.8 ± 2.4	28.3 ± 1.7	33.8 ± 1.8	38.2 ± 1.7	41.8 ± 1.6	47.0 ± 1.3	50.6 ± 1.2	56.1 ± 0.9	0.014
188		oxiranyl-methyl-hydroperoxide	-40.2 ± 0.9	82.3 ± 2.7	28.9 ± 2.0	34.9 ± 1.9	39.6 ± 1.7	43.2 ± 1.4	48.2 ± 1.1	51.6 ± 1.0	56.8 ± 0.8	0.013
189		3-hydroperoxy-propylperoxy ^a	-28.1 ± 0.9	98.0 ± 3.3	34.9 ± 1.2	40.1 ± 1.4	44.7 ± 1.5	48.5 ± 1.5	54.4 ± 1.5	58.7 ± 1.5	65.4 ± 1.1	0.026
190		1-methyl-2-hydroperoxy-ethylperoxy ^a	-31.2 ± 0.9	97.2 ± 3.6	36.2 ± 1.7	41.9 ± 1.4	46.3 ± 1.2	49.8 ± 1.1	55.1 ± 1.2	59.1 ± 1.3	65.5 ± 1.1	0.026
191		2-hydroperoxy-propylperoxy ^a	-31.1 ± 0.9	97.0 ± 3.6	36.5 ± 1.7	42.4 ± 1.7	47.2 ± 1.6	51.0 ± 1.4	56.5 ± 1.2	60.4 ± 1.1	66.3 ± 0.9	0.026
192		1,3-dihydroperoxy-prop-2-yl ^a	-15.6 ± 0.9	95.3 ± 3.9	38.2 ± 4.7	48.4 ± 3.6	54.4 ± 1.5	57.5 ± 0.2	60.5 ± -0.5	62.5 ± -0.2	66.3 ± 0.3	0.014
193		2,3-dihydroperoxy-propyl ^a	-15.8 ± 0.9	103.5 ± 3.1	35.6 ± 1.7	41.5 ± 1.8	46.2 ± 1.8	50.0 ± 1.6	55.5 ± 1.4	59.4 ± 1.3	65.3 ± 0.9	0.014
194		1,3-butadiyne	109.9 ± 0.4	58.9 ± 1.1	17.0 ± 1.0	19.7 ± 0.9	21.4 ± 0.8	22.8 ± 0.7	24.8 ± 0.7	26.3 ± 0.7	28.9 ± 0.5	0.014
195		but-3-yn-1-en-1-yl	130.2 ± 0.9	67.3 ± 1.1	17.2 ± 1.1	20.4 ± 1.1	22.8 ± 1.0	24.7 ± 1.0	27.5 ± 1.0	29.6 ± 0.9	32.9 ± 0.7	0.016

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	T1
196		but-1-yn-3-en-3-yl	118.7 ± 0.9	70.3 ± 1.2	18.7 ± 0.9	21.2 ± 0.9	23.3 ± 0.9	25.0 ± 0.9	27.6 ± 0.9	29.7 ± 0.9	32.9 ± 0.7	0.021
197		1-buten-3-yne	69.0 ± 0.9	66.2 ± 1.1	17.2 ± 1.2	20.9 ± 1.3	23.9 ± 1.3	26.3 ± 1.3	30.1 ± 1.3	32.8 ± 1.2	37.2 ± 0.9	0.013
198		1,2,3-butatriene	76.7 ± 0.9	65.2 ± 1.1	17.5 ± 1.1	21.0 ± 1.3	23.9 ± 1.3	26.3 ± 1.3	30.1 ± 1.3	32.9 ± 1.2	37.4 ± 0.9	0.015
199		1,2-butadien-1-yl	76.8 ± 0.9	71.9 ± 1.1	18.8 ± 1.2	22.6 ± 1.4	25.8 ± 1.5	28.5 ± 1.5	32.8 ± 1.5	36.1 ± 1.4	41.2 ± 1.1	0.020
200		1,3-butadien-2-yl	76.2 ± 0.9	69.6 ± 1.2	18.8 ± 1.4	23.1 ± 1.6	26.6 ± 1.6	29.5 ± 1.6	33.9 ± 1.5	37.2 ± 1.4	42.3 ± 1.1	0.015
201		1,3-butadien-1-yl	86.4 ± 0.9	68.3 ± 1.3	18.7 ± 1.8	23.7 ± 1.9	27.7 ± 1.7	30.7 ± 1.5	34.8 ± 1.2	37.7 ± 1.0	42.1 ± 0.8	0.015
202		1-butyne	40.1 ± 0.8	69.2 ± 1.3	19.5 ± 1.4	23.9 ± 1.6	27.7 ± 1.6	30.9 ± 1.7	35.9 ± 1.7	39.7 ± 1.6	45.8 ± 1.2	0.011
203		1,2-butadiene	38.5 ± 0.9	69.7 ± 1.2	18.9 ± 1.2	23.2 ± 1.6	27.0 ± 1.7	30.3 ± 1.8	35.6 ± 1.8	39.5 ± 1.7	45.8 ± 1.3	0.012
204		1,3-butadiene	26.5 ± 0.9	65.8 ± 1.3	18.5 ± 1.9	24.0 ± 2.3	28.7 ± 2.2	32.4 ± 1.9	37.6 ± 1.5	41.1 ± 1.3	46.6 ± 1.0	0.012
205		1-methylallyl	32.9 ± 0.9	72.0 ± 1.3	19.9 ± 1.4	24.8 ± 1.9	29.3 ± 2.0	33.1 ± 2.1	39.1 ± 2.0	43.6 ± 1.9	50.6 ± 1.5	0.013
206		2-methylallyl	33.3 ± 0.9	70.2 ± 1.2	19.6 ± 1.7	24.9 ± 2.0	29.5 ± 2.1	33.3 ± 2.1	39.2 ± 2.0	43.6 ± 1.9	50.6 ± 1.5	0.020
207		1-buten-1-yl	59.3 ± 0.9	74.5 ± 1.5	20.6 ± 1.4	25.4 ± 1.7	29.6 ± 1.8	33.2 ± 1.8	38.8 ± 1.8	43.1 ± 1.8	49.9 ± 1.4	0.014
208		3-buten-1-yl	49.8 ± 0.9	75.5 ± 1.4	20.7 ± 1.2	25.3 ± 1.6	29.5 ± 1.8	33.1 ± 1.9	38.7 ± 1.9	43.0 ± 1.8	49.8 ± 1.4	0.011
209		2-buten-2-yl	53.8 ± 0.9	74.4 ± 1.4	20.3 ± 1.0	24.5 ± 1.5	28.5 ± 1.8	32.1 ± 1.9	38.1 ± 2.0	42.6 ± 1.9	49.7 ± 1.5	0.014
210		1-butene	-0.0 ± 0.1	73.2 ± 1.5	20.8 ± 1.5	26.1 ± 1.9	30.9 ± 2.0	35.0 ± 2.1	41.5 ± 2.1	46.5 ± 2.0	54.4 ± 1.6	0.010
211		cis-2-butene	-1.5 ± 0.3	73.3 ± 1.3	20.3 ± 1.3	25.3 ± 1.9	30.0 ± 2.1	34.2 ± 2.3	41.0 ± 2.3	46.2 ± 2.2	54.2 ± 1.7	0.010
212		trans-2-butene	-2.7 ± 0.2	70.7 ± 1.5	21.1 ± 1.3	26.0 ± 1.7	30.5 ± 2.0	34.6 ± 2.1	41.2 ± 2.2	46.2 ± 2.1	54.2 ± 1.6	0.010
213		iso-butene	-4.1 ± 0.2	70.2 ± 1.5	21.1 ± 1.4	26.1 ± 1.8	30.8 ± 2.0	34.8 ± 2.1	41.3 ± 2.2	46.3 ± 2.1	54.3 ± 1.6	0.010
214		1-butyl	19.3 ± 0.9	78.5 ± 1.7	23.0 ± 1.6	28.5 ± 2.0	33.6 ± 2.2	37.9 ± 2.2	44.9 ± 2.2	50.2 ± 2.2	58.6 ± 1.7	0.010
215		2-butyl	16.6 ± 0.9	79.0 ± 1.5	21.9 ± 1.5	27.2 ± 2.0	32.3 ± 2.3	36.8 ± 2.4	44.0 ± 2.4	49.6 ± 2.3	58.3 ± 1.8	0.011

Table 3. continued

No.	Structure	Name	$\Delta_f H_{298}^0$ [kcal/mol]	S_{298}^0 [cal/mol/K]	$C_p(300\text{ K})$ [cal/mol/K]	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	Tl
216		iso-butyl	17.8 ± 0.9	76.4 ± 1.6	23.1 ± 1.8	28.9 ± 2.1	34.0 ± 2.2	38.3 ± 2.2	45.1 ± 2.2	50.3 ± 2.1	58.6 ± 1.7	0.010
217		tert-butyl	13.0 ± 0.9	76.2 ± 1.4	21.7 ± 1.1	26.6 ± 1.9	31.6 ± 2.3	36.1 ± 2.4	43.5 ± 2.5	49.2 ± 2.4	58.1 ± 1.8	0.011
218		n-butane	-30.0 ± 0.1	73.7 ± 2.0	24.0 ± 1.5	29.7 ± 2.0	35.2 ± 2.2	39.9 ± 2.3	47.7 ± 2.4	53.7 ± 2.4	63.1 ± 1.9	0.009
219		iso-butane	-32.0 ± 0.4	71.2 ± 1.9	23.9 ± 2.0	30.2 ± 2.3	35.8 ± 2.3	40.6 ± 2.3	48.1 ± 2.3	53.8 ± 2.3	63.0 ± 1.8	0.009

^aThese species used the MP2 correction, eq 2 for the complete basis set extrapolation.

analyses, with α uniformly distributed between 0 and 1. The results are summarized in Table 4.

Table 4. Uncertainty in the Standard-State Entropy, S_{298}^0
[All Units in cal/(mol K)]

no.	species	$\sigma_{\text{uncorrelated}}$	$\sigma_{\text{correlated}}$	$3\sigma_{\text{avg}}$	"worst case"
7	OH	0.1	0.1	0.2	0.1
40	vinyl	0.1	0.1	0.2	0.4
86	methyl formate	0.2	0.3	0.7	0.9
117	propene	0.2	0.4	0.8	0.9
140	3-oxetanyl	0.2	0.4	0.9	1.0
147	propylene oxide	0.2	0.5	1.0	1.1
162	2-propanol	0.3	0.7	1.5	1.6
189	3-hydroperoxyl-propylperoxy	0.6	1.8	3.5	3.3
196	but-1-yn-3-en-3-yl	0.2	0.5	1.0	1.1
218	n-butane	0.4	1.0	2.0	2.0

The standard deviation in S_{298}^0 for the uncorrelated MC analysis is listed in the third column, $\sigma_{\text{uncorrelated}}$; the same results for the correlated MC analysis are provided in the adjacent column, $\sigma_{\text{correlated}}$. The correct value is presumably somewhere between the two, because it is unlikely that all the ro-vibrational parameters are completely uncorrelated or completely correlated. The worst-case scenario is presented in the final column. The worst-case scenario results are close to the 2σ for the correlated MC analysis. Also presented for comparison is the average of the 3σ values, $3\sigma_{\text{avg}} \equiv (3\sigma_{\text{uncorrelated}} + 3\sigma_{\text{correlated}})/2$, which is even closer to the worst-case scenario. The results for the heat capacity were qualitatively similar, with the uncertainty increasing with the number of vibrational modes and decreasing with temperature. The uncertainty limits provided in Table 3 are reasonable, provided that the assumptions regarding independent partition functions are appropriate. For species with strong internal hydrogen bonding—such as hydroperoxylalkylperoxy radicals—or other species with highly anharmonic behavior, the uncertainties in Table 3 may be too small.

Comparison with Literature Values. Of the 219 molecules presented in Table 3, 134 of them are also found in the five most commonly used databases in combustion chemistry: Active Thermochemical Tables (ATcT),⁵ Third Millennium Thermodynamic Database (TMTD),⁶ NIST,² Baulch,³ and PrImE.⁴ To facilitate comparison among the databases, as well as to highlight any discrepancies, the results for these species are presented in Table 5. (Note that some of the values listed in the ATcT column are not yet in the official ATcT database but are snapshots of future ATcT values, as reported by Goos, Burcat, and Ruscic.⁶)

Analysis of Outliers. The Active Thermochemical Tables are the most reliable data for the enthalpy of formation, and the present work is in excellent agreement with the ATcT, because the BAC are referenced against these values. In comparison to the other databases, there are few molecular species for which there were significant differences. In some instances, the differences are due to fundamental errors in the source material that have propagated through multiple databases. The identification of an error in a database should not be construed as a criticism of that database's authors. Most databases are unevaluated compilations, and in any case the authors of databases should not be blamed if the origin of an error is an incorrect value or interpretation published by someone else. Database authors should be commended for providing a much needed service to the whole chemistry community. A discussion of noteworthy outliers is provided below.

Table 5. Comparison with Literature Values (When Available)

no.	name	$\Delta_f H_{298}^0$ [kcal/mol]						S_{298}^0 [cal/(mol K)]			
		present work	ATcT ⁵	TMTD ⁶	NIST ²	Baulch ³	PrIme ⁴	P.W.	NIST ²	Baulch ³	PrIme ⁴
1	H ₂	−0.0		0.0		0.0	0.0	31.1	31.2	31.2	31.2
2	CH (doublet)	142.3		142.4	142.0	142.5	142.8	43.6	43.7	43.7	43.7
3	CH ₂ (singlet)	102.5	102.5 ^a	102.5		102.4	102.7	45.1		45.1	45.2
4	CH ₂ (triplet)	93.8	93.6 ^a	93.5	92.3	93.3	93.5	46.6	46.4	46.6	46.5
5	methyl	35.2	35.0 ^a	35.1	34.8	35.0	35.1	46.4	46.4	46.4	46.4
6	methane	−17.6	−17.8	−17.8	−17.9	−17.9	−17.8	44.4	45.1	44.5	44.5
7	OH	8.9	9.0	8.9	9.3	8.9	9.4	43.9	43.9	43.9	43.9
8	H ₂ O	−58.0	−57.8	−57.8	−57.8	−57.8	−57.8	45.0	45.1	45.1	45.1
9	CO	−26.3	−26.4 ^a	−26.4	−26.4	−26.4		47.1	47.2	47.2	
10	HCO	10.2	10.0 ^a	10.1	10.4	10.3	10.0	53.5	53.7	53.6	53.6
11	formaldehyde	−26.2	−26.1 ^a	−26.1	−27.7	−26.0	−25.9	52.2	52.3	52.3	52.3
12	hydroxymethylene (singlet)	26.1	25.9 ^a	30.0				53.7			
13	hydroxymethylene (triplet)	51.8				49.3		58.3		57.4	
14	methoxy	4.9	5.2 ^a	5.0	4.1	4.1		54.4		54.8	
15	hydroxymethyl	−3.6	−3.9 ^a	−4.1	−2.0	−4.3	−3.5	58.2		58.3	58.3
16	methanol	−48.2	−48.0 ^a	−48.0	−49.0	−48.2	−48.0	57.2		57.3	57.3
17	O ₂	0.0		0.0		0.0	0.0	48.9	49.0	49.0	49.0
18	HO ₂	2.7	2.9	2.9	0.5	3.5	3.0	54.6	54.8	54.7	54.7
19	HOOH	−32.1	−32.4	−32.5	−32.5	−32.6	−32.5	55.8	55.7	56.0	56.0
20	CO ₂	−94.1	−94.0	−94.1	−94.1	−94.1	−94.0	51.0	51.1	51.1	51.1
21	hydroxycarbonyl	−43.7	−44.0	−43.3		−51.9	−43.3	60.2		60.2	60.2
22	formyloxy	−30.2	−29.9	−29.9		−36.0	−36.0	60.3		57.3	57.3
23	formic acid	−90.5	−90.5 ^a	−90.5	−90.5		−90.5	59.5	59.4		59.1
24	methylperoxy	3.3	2.9 ^a	2.9		4.8	2.1	64.4		64.5	64.4
26	methyl hydroperoxide	−30.7	−30.5 ^a	−30.3	−31.3	−33.0	−30.3	67.1		65.0	65.9
28	formylperoxy	−25.2				−9.0		66.2		71.4	
33	C ₂ (singlet)	197.6	198.0 ^a	197.6	200.2	200.2	197.0	45.5	47.7	45.7	47.1
34	C ₂ (triplet)	199.4		201.3		202.0		47.8		49.7	
35	ethynyl	135.7	135.7 ^a	135.8	114.0	135.3	135.3	51.6	49.6	51.0	51.0
36	acetylene	54.6	54.6 ^a	54.5	54.2	54.5	54.5	47.7	48.0	48.0	48.0
38	vinylidene (singlet)	98.4	98.5 ^a	98.5			99.1	54.5			52.8
40	vinyl	71.2	71.1 ^a	70.9	71.0	71.6	71.6	55.8		55.9	55.9
41	ethynylidyne (doublet)	120.4	121.6 ^a	121.6				54.3			
42	ethene	12.5	12.6 ^a	12.5	12.5	12.5		52.3	52.4	52.4	
44	ethyldiene (singlet)	87.5	87.7 ^a	87.7				57.9			
46	ethyl	28.9	28.7 ^a	28.6	28.4	28.9	28.4	59.1		59.1	59.1
47	ethane	−20.0	−20.0 ^a	−20.0	−20.0	−20.0	−20.0	54.7		54.7	54.8
49	C ₂ O (triplet)	91.0	90.6	90.5	68.5	91.6	69.6	55.8	55.7	55.7	55.8
50	ketenyl	42.9	42.5 ^a	42.6		41.9		58.8		58.6	
51	ethynol	22.0	22.2 ^a	22.3		22.3		59.1		59.5	
52	ketene	−11.7	−11.6		−20.9	−11.4	−11.4	57.6		57.8	57.8
55	oxiranyl	40.0		39.3			39.3	60.4			60.3
56	2-hydroxylvinyl	31.5				27.0		62.7		62.7	
58	vinoxyl	4.4		3.0		2.5		61.9		64.0	
59	acetyl	−2.3	−2.3 ^a	−2.5	−2.9	−2.4	−2.5	63.7		63.9	63.9
60	oxirane	−12.4	−12.6 ^a	−12.6	−12.6	−12.6	−12.6	57.9	58.1	58.0	58.0
61	ethenol	−29.9		−29.8	−30.6		−29.8	62.2			69.3
62	acetaldehyde	−39.6	−39.5 ^a	−39.7	−40.8	−39.7	−39.7	63.0		63.1	63.1
63	ethoxy	−3.1	−2.7 ^a	−2.7		−3.6	−3.3	66.8		65.6	66.3
64	methoxymethyl	0.8		0.2		0.0	0.2	67.3		67.4	67.3
65	2-hydroxyethyl	−5.9	−6.2 ^a	−6.2		−8.6	−5.7	69.4		65.7	69.7
66	1-hydroxyethyl	−13.0	−13.2 ^a	−13.2		−12.3	−12.9	68.1		67.1	69.1
67	ethanol	−56.4			−56.0	−56.2		66.8		67.1	
68	dimethyl ether	−43.9	−44.0 ^a	−44.0	−44.0	−44.0	−44.0	63.9		63.9	63.9
72	glyoxal	−50.9	−50.7 ^a	−50.7	−50.7	−50.7	−50.7	64.6		14.2	65.1
73	oxiranone (acetolactone)	−41.0		−42.5			−42.5	63.1			63.1
74	hydroxyketene	−36.2		−37.1				66.6			
75	ethynediol	−4.8		−6.7				67.4			
76	vinylperoxy	27.5				4.0		68.1		33.1	

Table 5. continued

no.	name	$\Delta_f H_{298}^0$ [kcal/mol]						S_{298}^0 [cal/(mol K)]			
		present work	ATcT ⁵	TMTD ⁶	NIST ²	Baulch ³	PrIMe ⁴	P.W.	NIST ²	Baulch ³	PrIMe ⁴
80	methoxylformyl	−37.6		−39.0				70.5			
82	acetyloxy	−44.9		−46.1				67.7			
85	acetic acid	−103.3	−103.3 ^a	−103.3	−103.5		−103.3	68.2	67.6		67.7
86	methyl formate	−85.6	−85.5 ^a	−85.5	−80.5			69.0			
89	ethylperoxy	−5.0		−6.9		−6.5	−6.9	74.2		75.0	71.7
90	hydroperoxyethyl	12.2				7.9		79.0		79.8	
96	ethyl hydroperoxide	−38.5		−38.7	−50.0	−41.1	−41.5	75.2		76.2	75.2
97	dimethyl peroxide	−29.1		−30.0	−30.0		−29.9	72.2			73.7
98	ketenylperoxy	19.2				−19.9		75.8		37.1	
99	acetylperoxy	−37.5				−41.8		76.2		76.4	
100	formylmethylperoxy	−18.9				−12.7		77.6		77.0	
106	HCCCH (singlet)	142.7		195.5			195.5	59.5			60.1
107	HCCCH (triplet)	130.5		171.9		180.5	180.5	63.8		62.3	62.3
108	propargyl	84.2	84.0 ^a	83.3	81.0	81.5		60.6		60.5	
109	allene	45.1	45.5 ^a	45.6		45.5	45.6	59.3		58.2	58.2
110	propyne	44.3	44.4 ^a	44.3	44.3	44.2	44.3	59.0		59.3	59.3
111	cyclopropene	67.6	67.9 ^a	67.9			66.2	58.0			58.2
112	allyl	40.6		39.1	40.9	40.8	39.1	61.5		62.0	61.9
113	cyclopropyl	69.9		66.9			66.9	61.6			60.1
114	1-methylvinyl	60.5		56.8			56.8	65.4			63.6
115	2-methylvinyl	64.1		63.5		62.8	63.5	64.9		64.8	64.8
116	cyclopropane	13.0	12.8 ^a	12.7	9.4	12.8	12.7	56.7		56.7	56.7
117	propene	4.6	4.8 ^a	4.8	4.9	4.8	4.8	63.6		63.7	63.7
119	<i>n</i> -propyl	24.3		24.2	23.9	24.0	24.2	69.3		69.2	69.4
120	isopropyl	21.2			22.0	21.5		68.9		69.1	
121	propane	−25.2	−25.0 ^a	−25.0	−25.0	−25.0		66.1		64.6	
122	HCCCO	69.1				88.9		66.4		63.7	
125	vinylformyl	23.2		21.2		17.3	21.2	67.9			71.8
128	acrolein	−15.5		−16.3		−17.9	−16.3	65.4		67.4	71.0
132	allyloxy	23.7				22.4		72.6		73.1	
133	propen-2-oxy	−6.9		−8.0			−8.0	72.9			73.5
135	oxiranylmethyl	26.0		24.9			24.9	69.9			70.1
138	propionyl	−6.9		−7.8		−7.7	−7.8	74.7		73.9	75.1
143	acetone	−52.0	−51.6 ^a	−51.3	−52.2		−51.3	70.9			70.6
144	propanal	−45.0		−44.3	−45.1	−44.4	−45.9	73.5	72.8	72.8	72.8
145	propen-1-ol	−35.8			−40.4			70.8			
146	propen-2-ol	−40.6			−42.1	−29.8		69.6		74.6	
147	propylene oxide	−22.3		−22.2	−22.6		−22.2	68.5	68.7		67.3
148	oxetane	−19.0		−19.4	−19.3		−19.4	65.6			65.6
149	allyl alcohol	−30.1		−29.6	−29.6			72.6			
150	cyclopropanol	−24.2		−24.3			−24.3	68.0			66.3
151	<i>n</i> -propoxy	−8.1		−8.5				75.7			
161	<i>n</i> -propanol	−61.3		−61.0	−61.2		−61.0	76.3	77.1		77.3
162	2-propanol	−65.4	−65.2 ^a	−65.2	−65.2		−65.2	74.2			73.9
163	ethyl methyl ether	−51.9			−51.7			73.5			
174	<i>n</i> -propylperoxy	−9.8		−10.1				83.5			
179	<i>n</i> -propyl-hydroperoxide	−43.3		−43.4	−60.0			84.2			
180	isopropyl-hydroperoxide	−47.7			−47.1			82.4			
194	1,3-butadiyne	109.9	110.0 ^a	109.5	111.0	111.7	109.5	59.1		59.8	59.6
195	but-3-yn-1-en-1-yl	130.2		129.8		127.1	129.8	67.3		68.0	67.3
196	but-1-yn-3-en-3-yl	118.7		119.9				70.3			
197	1-buten-3-yne	69.0				68.0		66.2		66.7	
199	1,2-butadien-1-yl	76.7		76.1			75.6	71.9			70.2
200	1,3-butadien-2-yl	76.8		75.3		74.0	75.3	69.6		68.6	70.2
201	1,3-butadien-1-yl	86.4		86.8		86.1	86.8	68.3		69.1	72.5
202	1-butyne	40.1	39.5 ^a	39.5	39.5		39.5	69.2			69.6
203	1,2-butadiene	38.5			38.8			69.7			
204	1,3-butadiene	26.5		26.5	26.0	26.3	26.5	65.8		66.5	70.1
205	1-methyl-allyl	32.9				33.4	32.5	72.0		68.9	73.1

Table 5. continued

no.	name	$\Delta_f H_{298}^0$ [kcal/mol]						S_{298}^0 [cal/(mol K)]			
		present work	ATcT ⁵	TMTD ⁶	NIST ²	Baulch ³	PrIme ⁴	P.W.	NIST ²	Baulch ³	PrIme ⁴
206	2-methyl-allyl	33.3		32.9				70.2			
207	1-buten-1-yl	59.3		58.8		59.1	58.8	74.5		74.9	74.4
208	3-buten-1-yl	49.8		48.9		51.3	48.9	75.5		75.6	75.8
209	2-buten-2-yl	53.8		53.5		54.2	53.5	74.4		72.5	74.9
210	1-butene	−0.0	0.0 ^a	0.0	−0.2	0.0		73.2		73.6	
211	<i>cis</i> -2-butene	−1.5	−1.8 ^a	−1.8	−1.8	−1.7		73.3		71.9	
212	<i>trans</i> -2-butene	−2.7	−2.7 ^a	−2.7	−2.6	−2.7		70.7		70.7	
213	isobutene	−4.1	−4.2 ^a	−4.2	−4.3	−4.0		70.2	70.2	70.9	
214	1-butyl	19.3		19.6		19.2	19.5	78.5		79.3	73.5
215	2-butyl	16.6		16.8	16.0		16.8	79.0			76.9
216	isobutyl	17.8		17.6	17.0	17.4	17.6	76.4		76.4	72.8
217	<i>t</i> -butyl	13.0		13.2	11.0	12.3	13.2	76.2		75.8	77.0
218	<i>n</i> -butane	−30.0	−30.1 ^a	−30.1	−30.1	−30.1	−30.1	73.7		74.0	74.0
219	isobutane	−32.0	−32.4 ^a	−32.3	−32.1	−32.2	−32.3	71.2		70.6	70.6

^aValue from an ATcT snapshot in ref 6.

•14, methoxy: The heat of formation for methoxy, $\Delta_f H_{298}^0 = 4.9$ kcal/mol, is in close agreement with the values in ATcT and TMTD, 5.2 and 5.0 kcal/mol, respectively. Accurate evaluation of the thermochemistry for methoxy is complicated by the presence of Jahn–Teller distortion and spin–orbit coupling in the ground electronic state, which is neglected in the present work. Marenich and Boggs recently calculated the partition function for methoxy by explicit summation of the eigenenergies of a spin-vibronic Hamiltonian that included these effects.²⁶ The change in enthalpy going from zero Kelvin to the standard state, $H(298\text{K}) - H(0\text{K})$, was calculated using both the spin-vibronic Hamiltonian and the less-accurate standard RRHO model, and the difference in ΔH between the two models was 0.1 kcal/mol. Similarly, the RRHO model underestimated the heat capacity at 298 K by $\sim 4\%$. Using the more sophisticated model, Marenich and Boggs determined a heat of formation $\Delta_f H_{298}^0 = 5.6 \pm 0.2$ kcal/mol.

•21, hydroxycarbonyl (HOCO): The heat of formation for *trans*-HOCO obtained in this work, -43.7 kcal/mol, is nearly 8 kcal/mol higher than the value reported by Baulch, which comes from an experiment by Fulle investigating the process $\text{OH} + \text{CO} \rightleftharpoons \text{HOCO} \rightarrow \text{H} + \text{CO}_2$.²⁷ However, the present work compares more favorably with other published values. The TMTD reports a value of -43.3 kcal/mol, based upon G3B3 calculations performed by Burcat, and the ATcT snapshot is -44.0 kcal/mol. An experimental study by Ruscic and Litorja²⁸ suggests a value $\geq -46.5 \pm 0.7$ kcal/mol. A computational investigation by Janoschek and Rossi using G3MP2B3⁸ suggests a value of -44.3 kcal/mol for the *trans* isomer, and subsequent high-accuracy CCSD(T)-CBS (W1U) calculations from Janoschek and Fabian²⁹ yield a value of -44.4 kcal/mol. Thus, it appears that the tabulated Baulch value is inaccurate, and the RQCISD(T) value obtained here is consistent with more recent values.

•22, formyloxy: The present value for the heat of formation, -30.2 kcal/mol, is 5 kcal/mol higher than the value reported in Baulch and PrIme, both of which were taken from calculations done by Burcat, based upon group additivity, in the 2002 iteration of his Ideal Gas Thermochemical Database. Similarly, the present value for the entropy, 60.3 cal/(mol K), is 3 entropy units higher than the group additivity estimates reported in the databases. Our results are in close agreement with the ATcT and latest version of the TMTD, -29.9 kcal/mol. These updated results were based upon high-level ab initio (W1U) calculations

of the CHO_2 potential energy surface from Fabian and Janoschek.²⁹ Accurate determination of the thermochemistry for formyloxy is complicated by the presence of a low-lying electronically excited state. Fabian and Janoschek computed $\Delta_f H_{298}^0 = -30.5$ kcal/mol for the $^2\text{A}_1$ ground state, and $T_0 = 1.7$ kcal/mol for the $^2\text{B}_2$ first electronically excited state (relative to the ground state). We also computed the thermochemistry for the $^2\text{B}_2$ state and obtained $T_0 = 1.3$ kcal/mol. Neumark and co-workers observed formyloxy using photoelectron spectroscopy.³⁰ Interpreting those results, Fabian and Janoschek estimated the experimental values of $\Delta_f H_{298}^0 = -31 \pm 3$ kcal/mol and $T_0 = 0.6$ kcal/mol, which would rule out the group-additivity values in Baulch and PrIme. The C_{2v} structures in both the $^2\text{A}_1$ and $^2\text{B}_2$ states are quite similar, and our computed heat capacities differed by less than 20% over the temperature range 300–2000 K. Consequently, the thermodynamic parameters reported in Table 3 and in the accompanying NASA polynomials assume that the rotational and vibrational contributions are unaffected by the electronic excitation (i.e., $Q_{\text{trans}}Q_{\text{rot}}Q_{\text{vib}}$ are equal to the ground-state parameters), and only the electronic partition function is affected ($Q_{\text{elec}} = 2 + 2e^{-T_0/k_B T}$).

•28, formylperoxy: The heat of formation value reported here, -25.2 kcal/mol, is lower than the value reported by Baulch by nearly 16 kcal/mol, which was based upon group-additive values for the parent molecule, formyl hydroperoxide. The present value is in close agreement with result based on Benson group additivity with hydrogen bond increments: -25.4 kcal/mol. Additionally, work by Benassi and Taddei produced several estimates ranging from -20 ± 1 to -22.1 kcal/mol,³¹ also much closer to the value reported here. The entropy reported here is also 5.2 cal/(mol K) lower than that reported in Baulch.

•35, ethynyl (HC_2): The present value, 135.7 kcal/mol, is 23 kcal/mol higher than the value in NIST, which is taken from the NIST-JANAF tables.³² However, NIST also lists a value from Tsang, 133 kcal/mol.³³ The other major databases all list values between 135 and 136 kcal/mol, in reasonable agreement with the present work.

•49, C_2O (triplet): The values from NIST and PrIme for $^3\text{C}_2\text{O}$ are more than 20 kcal/mol lower than the value obtained in this work, 91.0 kcal/mol. However, the TMTD points out that lower values for this species have been shown to be inaccurate in work by Neumark and co-workers³⁴ and by Williams and

Fleming.³⁵ The values in ATcT, TMTD, and Baulch are much closer to the present work: 90.6, 90.5, and 91.6 kcal/mol, respectively.

•50, ketenyl: The value reported for ketenyl, 42.9 kcal/mol, is in good agreement with the ATcT value of 42.5 kcal/mol. The ATcT value is derived from Szalay et al., who report $\Delta_f H_0^\circ = 42.3$ kcal/mol, on the basis of high-level ab initio calculations and heats of formation³⁶ (for comparison, we determined $\Delta_f H_0^\circ = 42.9$ kcal/mol prior to application of the BAC). More accurate calculation of the heat of formation is complicated by the fact that ketenyl is a $^2\Pi$ Renner–Teller molecule. The more stable structure is a $^2A''$ (trans)-bent geometry, with the radical site located on the terminal carbon. When the radical site is located on the oxygen, the structure is linear, which leads to the splitting of the two degenerate π orbitals (resulting in $^2A''$ and $^2A'$ electronic states). Both the present work and the calculations performed by Szalay et al. are for the more stable, nonlinear structure. Recently Allen and co-workers performed focal point analysis to determine the barrier to linearity from the bent geometry;³⁷ they determined a barrier of 1.8 ± 0.1 kcal/mol. Ketenyl is primarily of interest in acetylene oxidation ($C_2H_2 + O \rightarrow HCCO + H$, followed by $HCCO + O_2 \rightarrow$ products and $HCCO + NO_2 \rightarrow$ products), and hence is important for all high-temperature combustion mechanisms. In this context, it is accurate determination of the bent structure that is critical, because the consumption reactions proceed via addition to the carbon-centered radical site.³⁸

•52, ketene: The value reported in this work, -11.7 kcal/mol, is about 10 kcal/mol higher than the value reported here from the NIST WebBook, which comes from work by Orlov et al.³⁹ However, there are other values reported in the WebBook, including the value of -11.4 ± 0.4 kcal/mol from work by Nuttall, Laufer, and Kilday.⁴⁰ Also, the present work compares favorably with W1U calculations performed by us, which yielded a value of -12.3 kcal/mol (or -12.5 kcal/mol with an anharmonicity correction). Finally, the values in ATcT, TMTD, Baulch, and PrIme are all within 0.8 kcal/mol of the present work.

•56, 2-hydroxylvinyl (CHCHOH): Although the value reported here, 31.5 kcal/mol, differs from the Baulch value by just over 5 kcal/mol, it is in close agreement with the group additivity value, 29.5, as well as published values by da Silva et al. for the syn conformer: 28.7 (B3LYP), 31.1 (CBS-APNO), and 31.4 (G3 and CBS-Q) kcal/mol.⁴¹ It is noted that the result from this work is based on the “syn” conformer, and three higher energy conformers were also identified.

•72, glyoxal: The value reported in Baulch for S_{298}° is 59.54 J/(mol K), which we presume to be a typographical error. Given the size of the molecule, the entropy is expected to be between 200 and 300 J/(mol K). If the intended value were 259.54 J/(mol K) (62.0 cal/(mol K)), then agreement with the present work is within 2.6 cal/(mol K).

•76, vinylperoxy: The enthalpy reported here, 27.5 kcal/mol, differs from the Baulch value by 24 kcal/mol, which was based upon group-additive values for the parent molecule, vinyl hydroperoxide. The present value is in much closer agreement with the group additivity value of 29.7 kcal/mol, as well as published values of 24.5⁴² and 24.3 kcal/mol⁴³ as compiled by Sebbar et al.⁴⁴ The entropy reported here, 68.1 cal/(mol K), is 35 cal/(mol K) higher than in Baulch. Note that the entropy for vinylperoxy reported in Baulch is actually lower than the values reported for vinyl and vinoxy, which does not make physical

sense. For these reasons, we believe there was an error in the derivation of the entropy and enthalpy values in Baulch.

•86, methyl formate: The value reported in this work, -85.6 kcal/mol, is 5 kcal/mol higher than the value reported in the NIST WebBook, from work by Gladil et al.⁴⁵ However, there are other values reported in the WebBook: -83.41 kcal/mol from Guthrie,⁴⁶ -86.6 kcal/mol from Hine and Klueppel,⁴⁷ and -84.97 kcal/mol from Hall and Baldt.⁴⁸ The present value is in excellent agreement with the results from ATcT and TMTD.

•96, ethyl hydroperoxide: The value reported here, -38.5 kcal/mol, is 12 kcal/mol higher than the value from the NIST WebBook. The NIST values are derived from work by Stathis and Egerton,⁴⁹ which were “preliminary” results from bomb calorimetry experiments performed in 1939. More recent estimates agree more favorably with the value reported here: a value of -41.5 kcal/mol was obtained from ab initio calculations by Lay et al.,⁵⁰ and the TMTD reports a value of -38.7 kcal/mol obtained from G3B3 calculations by Burcat.

•98, ketenylperoxy: The value here, 19.2 kcal/mol, differs from the Baulch value by 40 kcal/mol. The value in Baulch was obtained by group additivity of the parent molecule, hydroperoxyketene, which was then corrected by applying an H-bond increment method. However, the standard enthalpy of formation predicted by group additivity for ketenylperoxy is 23.6 kcal/mol. We are not aware of any other published estimates for the heat of formation of this compound. One explanation for the discrepancy with Baulch is the possibility of a transcription error. The value reported in Baulch is -83.29 kJ/mol. If the intended value were $+83.29$ kJ/mol (19.9 kcal/mol), then the agreement with the present work would be within 1 kcal/mol. Given the reasonable agreement between the present work and Baulch for HCCO (43.2 and 41.9 kcal/mol, respectively), a transcription error seems plausible. It also bears mentioning that the T1 diagnostic for ketenylperoxy is unusually high, 0.043, which suggests that there is considerable uncertainty in our value due to multireference effects. However, we would speculate that the uncertainty is on the order of ± 5 kcal/mol, and not ± 40 kcal/mol. Nonetheless, given the importance of this radical in acetylene combustion chemistry (via HCCO oxidation), we recommend that multi-reference calculations be performed to reduce the uncertainty. The entropy reported in Baulch is 38.7 cal/(mol K) lower than the present work. Much like their values for vinyl and vinylperoxy, the reported entropy for ketenylperoxy is considerably lower than their value for ketenyl, which does not make physical sense.

•99, acetylperoxy: The value here, -37.5 kcal/mol, differs from the Baulch value by nearly 5 kcal/mol. However, the group additivity estimate for acetylperoxy is -38.5 kcal/mol, and the G3MP2B3 result of -38.0 kcal/mol from Janoschek and Rossi⁸ is in close agreement.

•100, formylmethylperoxy: The value here, -18.9 kcal/mol, differs from the Baulch value by over 6 kcal/mol. The group additivity estimate for vinoxyperoxy is -20.0 . Additionally, Lee and Bozzelli⁵¹ used CBS-Q to obtain -21.01 kcal/mol.

•107, HCCCH: The standard heat of formation of triplet HCCCH obtained here, 130.5 kcal/mol, is lower than the TMTD, Baulch, and PrIme values by 50 kcal/mol. However, the value in this work is in much better agreement with high-level CCSD(T) calculations by Lau and Ng, who computed a value of 132.2 kcal/mol;⁵² Lau and Ng also cite a value of 127.2 ± 4.1 kcal/mol derived from experiments by Prodnuk et al.⁵³ Further investigation of the PrIme value suggests that it (and presumably the Baulch value as well) was obtained by combining the (ZPE-corrected) relative energy of propargyl and $H + HCCCH$

(triplet) (92.8 kcal/mol) as reported by Vereecken et al.⁵⁴ with the heat of formation of propargyl at 0 K (87.71 kcal/mol) as reported by Kiefer et al.⁵⁵ However, in addition to neglecting thermal contributions, this calculation appears to neglect the H atom, whose heat of formation should be subtracted from their result. Subtracting the heat of formation for a hydrogen atom at 0 K (51.633 kcal/mol, as reported in ATcT) from this result produces a heat of formation for HCCCH (triplet) at 0 K of 128.9 kcal/mol, which is in much better agreement with the value at 298 K reported here (and by Lau and Ng). This apparent error likely affects the reported values for singlet HCCCH in these references.

•108, propargyl: The current value for propargyl is 84.2 kcal/mol, which is in good agreement with the ATcT but is 3.2 kcal/mol larger than the value reported in NIST (which comes from Tsang³³), and 0.9 kcal/mol larger than the value reported in Baulch (which comes from Kerr and Stocker⁵⁶); both of those values are derived from experiments by Tsang in 1978.⁵⁷ The value in TMTD, 83.3 kcal/mol, is from G3B3 calculations performed by Burcat. The available experimental and theoretical thermochemistry for propargyl is reviewed by Vázquez et al.⁵⁸ We believe that their recommended value, $\Delta_f H_{298}^0 = 84.1$ kcal/mol, is the most accurate value to date for this important radical.

•114, 1-methylvinyl: The value reported in this work for 1-methylvinyl (or propen-2-yl), 60.5 kcal/mol, is 4 kcal/mol higher than the value from the PrIme database, which comes from work by Wu and Kern.⁵⁹ Wu and Kern estimated the heat of formation for 1-methylvinyl from thermal dissociation of propene, assuming that the C–H bond strength on the C2 was the same for propene as for ethene. The standard enthalpy of formation predicted by group additivity is 61.6 kcal/mol. A B3LYP value of 58.9 kcal/mol was calculated by Sebbar et al.,⁶⁰ and Ponomarev and Takhistov suggest a value of 56.5 kcal/mol.⁶¹ CBS-QB3 calculations (with the harmonic oscillator approximation) by our group suggest a value of 61.3 kcal/mol. Thus, there are a range of justifiable estimates for this compound, and the value obtained in this work using RQCISD(T) appears to be within that range.

•122, HCCCO: The current value for the standard-state enthalpy of formation is 69.1 kcal/mol, which is nearly 20 kcal/mol lower than the value recommended by Baulch. The Baulch recommendation is taken from Tomašić and Scuseria,⁶² who computed the binding energy for $\text{HC}_2 + \text{CO} \rightarrow \text{HCCCO}$ at the CISD/TZ2P level theory. The enthalpy of formation in Baulch for HCCCO was then estimated from the tabulated results for HC_2 and CO. Hansen et al.⁶³ report a value of $\Delta_f H_{0\text{K}}^0$ of 70.3 kcal/mol, which is in good agreement with the value of $\Delta_f H_{0\text{K}}^0$ of 70.1 kcal/mol (prior to BAC correction) reported here. Higher level computational methods were used in ref 63 and in the present work, so these results are expected to be more reliable than the methods used in the earlier work by Tomašić and Scuseria.⁶² The same source was used for the entropy in Baulch, which is 2.7 cal/(mol K) lower than in the present work, 66.4 cal/(mol K).

•145, propen-1-ol: The value reported in this work for *trans*-propen-1-ol, −35.8 kcal/mol, is almost 5 kcal/mol higher than the value from the NIST WebBook, which comes from work by Turecek.⁶⁴ A similar discrepancy was noted and discussed by Khan et al. in their analysis of *trans* propen-1-ol using the G3//B3LYP method;⁹ they had obtained a value of −35.5 kcal/mol, in close agreement with the value obtained here.

•146, propen-2-ol: The value reported in this work for propen-2-ol, −40.6 kcal/mol, is more than 10 kcal/mol lower than the

value from Baulch. However, it agrees much more favorably with the value obtained via group additivity, −38.8 kcal/mol, and the value shown from the NIST WebBook, −42.1 kcal/mol, which comes from Turecek and Havlas.⁶⁵ Additionally, there is another value in the NIST WebBook of -38 ± 2 kcal/mol from Holmes and Lossing.⁶⁶ The value from this work is also in good agreement with the value of −40.1 kcal/mol from CBS-Q calculations by Morales and Martínez.⁶⁷

•179, *n*-propyl hydroperoxide: The value reported here, −43.3 kcal/mol, is over 16 kcal/mol higher than the value from the NIST WebBook. As with ethyl hydroperoxide, the NIST values are derived from work by Stathis and Egerton,⁴⁹ which were “preliminary” results from bomb calorimetry experiments performed in 1939. The present work compares more favorably with Burcat’s G3B3 estimate of -43.4 ± 2.0 kcal/mol in the TMTD.

•195, but-3-en-1-yn-1-yl: The result reported here for but-3-en-1-yn-1-yl, 130.2 kcal/mol, exceeds the recommended value from Baulch by 3 kcal/mol. The TMTD provides several additional estimates, including (i) G3B3 calculations from Burcat (which are the source of the PrIme value cited here) with a standard heat of formation of 129.8 kcal/mol for the E/*trans* isomer, and (ii) G3 calculations from Krokidis et al. giving 131.4 kcal/mol for the *trans* isomer.⁶⁸ Diffusion Monte Carlo (DMC) calculations from Krokidis et al. have suggested a significantly lower value of 126.0 kcal/mol for the *trans* isomer.⁶⁸ However, more recent work with high-level ab initio methods has suggested that the DMC result is inaccurate; calculations from Klippenstein and Miller (considering a C_4H_3 potential energy surface with both *cis* and *trans* isomers) suggest values of 130.8 kcal/mol (QCISD(T)) and 131.9 kcal/mol (MRCI(9e,9o)).⁶⁹ Focal-point analysis from Wheeler et al. suggests a value of 130.8 kcal/mol for the *trans* isomer.⁷⁰ The reader is referred to the papers by Klippenstein and Miller⁶⁹ and by Wheeler et al.⁷⁰ for a more complete discussion of their high-accuracy results and the sources of inaccuracy in other approaches.

■ CONCLUSION

High ab initio accuracy thermochemical parameter estimates for $\Delta_f H^0(298\text{K})$, $S^0(298\text{K})$, and C_p , based on RQCISD(T) calculations are presented for 219 small molecules relevant in combustion chemistry. For many of the molecules, these results represent the highest level calculations that have been reported. A comparison with values in published databases demonstrates the level of accuracy that can be achieved by this approach. On the basis of comparison to the Active Thermochemical Tables, the 3σ uncertainty in $\Delta_f H^0(298\text{K})$ is 0.9 kcal/mol. An analysis of discrepancies between the values reported here and database values provides some interesting insights. For 24 species, disagreements in $\Delta_f H_{298}^0$ in excess of 5 kcal/mol or ΔS_{298}^0 in excess of 5 cal/(mol K) were found. For most of these discrepancies, a careful review of the literature reveals alternative, often more recent, estimates that are more consistent with the RQCISD(T) value obtained in this work. The very large discrepancies for HCCCH (singlet and triplet), vinylperoxy, ketenylperoxy, and glyoxal appear to be due to simple mistakes or transcription errors in published databases.

■ ASSOCIATED CONTENT

§ Supporting Information

The thermochemistry for all 219 species are provided in a CHEMKIN-compatible NASA polynomial format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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■ ACKNOWLEDGMENTS

This work is supported by Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Science (BES) of the U.S. Department of Energy (DOE) through contract DE-FG02-98ER14914, and by Award No. KUS-II-010-01, made by King Abdullah University of Science and Technology (KAUST). C.F.G. gratefully acknowledges fellowship support from the National Science Foundation and the Alexander von Humboldt Foundation.

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