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Accurate Heats of Formation of the “Arduengo-Type” Carbene and Various Adducts Including H_2 from ab Initio Molecular Orbital Theory

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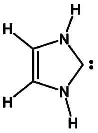
The heats of formation of saturated and unsaturated diaminocarbenes (imadazol(in)-2-ylidenes) have been calculated by using high levels of ab initio electronic structure theory. The calculations were done at the coupled cluster level through noniterative triple excitations with augmented correlation consistent basis sets up through quadruple. In addition, four other corrections were applied to the frozen core atomization energies: (1) a zero point vibrational correction; (2) a core/valence correlation correction; (3) a scalar relativistic correction; (4) a first-order atomic spin−orbit correction. The value of ΔH_f^{298} for the unsaturated carbene **1** is calculated to be 56.4 kcal/mol. The value of ΔH_f^{298} for the unsaturated triplet carbene ^{3}**1** is calculated to be 142.8 kcal/mol, giving a singlet−triplet splitting of 86.4 kcal/mol. Addition of a proton to **1** forms **3** with $\Delta H_f^{298}(\mathbf{3}) = 171.6$ kcal/mol with a proton affinity for **1** of 250.5 kcal/mol at 298 K. Addition of a hydrogen atom to **1** forms **4** with $\Delta H_f^{298}(\mathbf{4}) = 72.7$ kcal/mol and a C−H bond energy of 35.8 kcal/mol at 298 K. Addition of H^- to **1** gives **5** with $\Delta H_f^{298}(\mathbf{5}) = 81.2$ kcal/mol and **5** is not stable with respect to loss of an electron to form **4**. Addition of H_2 to the carbene center forms **6** with $\Delta H_f^{298}(\mathbf{6}) = 41.5$ kcal/mol and a heat of hydrogenation at 298 K of −14.9 kcal/mol. The value of ΔH_f^{298} for the saturated carbene **7** (obtained by adding H_2 to the C═C bond of **1**) is 47.4 kcal/mol. Hydrogenation of **7** to form the fully saturated imidazolidine, **8**, gives $\Delta H_f^{298}(\mathbf{8}) = 14.8$ kcal/mol and a heat of hydrogenation at 298 K of −32.6 kcal/mol. The estimated error bars for the calculated heats of formation are ±1.0 kcal/mol.

Introduction

There has been real excitement due to the discovery that stable carbenes (imidazol-2-ylidenes and/or imidazolin-2-ylidnenes, often called the “Arduengo-type” carbene)[1] can be made and stored for long times.[2−4] This has led to a significant increase in the use of these species for a wide range of chemical applications,[5−13] for example, as ligands to transition metals involved in homogeneous catalysis. In developing new uses for such species, it is important to have basic thermodynamic information about their stability. However, for the simplest unsubstituted model compound **1**, which can then be used as a basis for the prediction of heats of formation of substituted species through the use of appropriately chosen isodesmic reactions, the heat of formation is not available. In addition, the ability of the carbene to bind other species is of interest, e.g., a proton to determine its basicity, a hydride, or H_2.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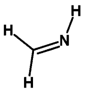
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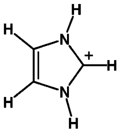
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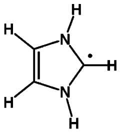
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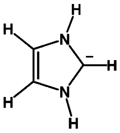
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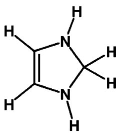
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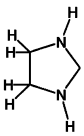
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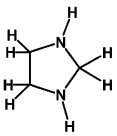
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A number of computational studies of carbenes based on the original discovery and our own follow-on computational studies,[14−17] have been reported. The hydrogenation energies of the unsaturated carbenes and their homologues (with C:, Si:, and Ge: at the carbene center) have been calculated at the MP4/6-311G(d,p)//MP2/6-31G(d) level and the geometries of the saturated carbenes with the same elements at the carbene center have been reported.[18] The role of aromaticity in the carbenes has been studied at the MP4/6-31G(d) level.[19] The mechanism for insertion of the carbene and their homologues into CH_4 has been studied at the B3LYP and CCSD(T) levels.[20] The interaction of a variety of carbenes with $Cr(CO)_5$ has been studied and compared to phosphines[21] at the B3LYP level following on earlier studies of the interaction of carbenes with $W(CO)_5$.[22] The dimerization energies of a number of these carbenes have been studied at the B3LYP level.[23] The proton affinities for a number of substituted carbenes have been obtained at the CBS-QB3 level and pK_a’s in a variety of solutions were also predicted.[24]

In addition to the chemical interest in such species, there is also substantial interest in the development of new materials to store hydrogen.[25] We propose, on the basis of our calculated energetics, that such carbenes may be useful as hydrogen storage materials. On the basis of our analysis as well as that of others, it is clear that one needs to have compounds that can add and release hydrogen near room temperature with free energies of reaction that are near zero. This is required to manage the pressure of the hydrogen that is released as well as to keep costs for regeneration of the hydrogenated species (readdition of H_2) at an energetic cost that can be managed.

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We have been associated with a group that has been developing an approach[26−38] to the reliable calculation of molecular thermodynamic properties, notably heats of formation, based on ab initio molecular orbital theory. Our approach is based on calculating the total atomization energy of a molecule and using this with known heats of formation of the atoms to calculate the heat of formation at 0 K. This approach starts with coupled cluster theory, including a perturbative triples correction (CCSD(T)),[39−41] combined with the correlation-consistent basis sets[42,43] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. Finally, one must include the zero point energy obtained from experiment, theory, or some combination. The standard heats of formation of compounds at 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions.[44]

We have applied this approach to predict the heat of formation of the model carbene **1**. To develop a scaling procedure for calculating the zero point energy, we also calculated the heat of formation of the simplest imine, CH_2NH, **2**, by using the same approach. Our result can be compared with the heat of formation recently calculated at the W2 level[45] by Martin and co-workers[46] who calculated the zero point energy from an anharmonic force field. The recent paper by Martin and co-workers provides a detailed discussion of various aspects of the structures, frequencies, and heat of formation of **2**. We have also calculated the energy of the first excited triplet state of the carbene, ^{3}**1**. We have further calculated the heat of formation of the compounds formed by adding H^+ to **1** to form **3**, H to **1** to form **4**, H^- to **1** to form **5**, and H_2 to **1** to form **6**. In addition, we have calculated the ability of the carbene to add H_2 to the double bond to form the saturated carbene **7** and the ability of the saturated carbene to add H_2 to the carbene center to form **8**. For comparison purposes, we note that we find errors under 1 kcal/mol in using our approach to calculate the heat of formation of C_2H_4, CH_2 ($^3B_1$ and $^1A_1$), and NH_3.[32,34]

Computational Approach

For the current study, we used the augmented correlation consistent basis sets aug-cc-pVnZ for H, C, and N (n = D, T, Q).[47] Only the spherical components (5d, 7f, and 9g) of the Cartesian basis functions were used. All of the current work was performed with the molpro suite of programs,[48] the Gaussian suite of programs,[49] and the NWChem suite of programs.[50] All of the calculations were done on a massively parallel HP Linux cluster with Itanium-2 processors in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory (MOLPRO and NWChem) or on a 16 processor SGI computer system (Gaussian and MOLPRO).

TABLE 1: Calculated Imine 2 Geometry Parameters[a]

parameter	MP2/ cc-pVTZ	CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ cc-pVQZ[46]	expt[61]
C=N	1.275	1.292	1.274	1.273
CH1	1.086	1.101	1.087	1.09
CH2	1.090	1.105	1.092	1.09
NH	1.020	1.032	1.020	1.021
H1CN	118.5	118.5	118.7	117.9
H2CN	124.7	124.5	124.6	125.1
HNC	109.5	109.5	109.9	110.4

[a] Bond distances in Å and bond angles in degrees.

The geometries were optimized at the frozen core MP2 level[51] with the cc-pVTZ correlation-consistent basis set. The vibrational frequencies were calculated at the MP2/cc-pVTZ level except for those radicals (see below) that were calculated after reoptimization at the density functional theory level, B3LYP/DZVP2.[52,53] For the imine, **2**, the geometries and frequencies were also calculated at the CCSD(T)/aug-cc-pVDZ level. The MP2/cc-pVTZ geometries were used in single point CCSD(T)/aug-cc-pVnZ calculation, n = D, T, Q calculations for both **1** and **2** to determine the valence correlation energy. We also used the CCSD(T)/aug-cc-pVDZ geometry for **2** to predict its valence correlation energy. The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[54,55] The orbitals were not symmetry equivalenced in the atomic calculations. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \qquad (1)$$

with $n = 2$ (DZ), 3 (TZ) and 4 (QZ), as first proposed by Peterson et al.[56] This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment by a small measure as compared to other extrapolation approaches up through $n = 4$.[27]

Core−valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[57] 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.[58] Most electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. For N in the ^4S state, no such correction is needed, but a correction is needed for the ^3P state of C. To correct for this effect, we apply an atomic spin−orbit correction of 0.08 kcal/mol for C on the basis of the excitation energies of Moore.[59]

By combining our computed $\sum D_0$ values with the known heats of formation[60] at 0 K for the elements ($\Delta H_f°(N) = 112.53$ kcal mol^{-1}, $\Delta H_f°(C) = 169.98 \pm 0.1$ kcal mol^{-1}and $\Delta H_f°(H) = 51.63$ kcal mol^{-1}), we can derive $\Delta H_f°$ values 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.[44]

Results and Discussion

The calculated geometry parameters for the imine **2** are given in Table 1 and those for the other molecules in Table 2. The calculated vibrational frequencies for the imine **2** are reported in Table 3 and for the remaining molecules in Table 4. The geometry for CH_2NH is in excellent agreement with the experimental structure[61] and with the high level CCSD(T)/aug-cc-pVQZ structure calculated by Martin et al.[46] The calculated frequencies at the CCSD(T)/aug-cc-pVDZ level for CH_2NH are in qualitative agreement with the experimental values[62] considering the differences between harmonic and anharmonic frequencies. Comparison of our CCSD(T) values with those of Martin and co-workers[46] using the cc-pVTZ basis set shows good agreement within 20−40 cm^{-1}. The MP2/cc-pVTZ frequencies are larger than the CCSD(T)/aug-cc-pVDZ values.

TABLE 2: Calculated Carbene and Associated Molecule Geometry Parameters[a]

parameter	**1**	^{3}**1**	**3**	**4**
:C−N	1.366	1.409 (1.418)	1.335	1.418 (1.433)
═C−N	1.380	1.419 (1.428)	1.372	1.394 (1.407)
C═C	1.362	1.346 (1.354)	1.368	1.351 (1.353)
═CH	1.074	1.076 (1.082)	1.074	1.075 (1.080)
:C−H			1.075	1.086 (1.093)
NH	1.004	1.016 (1.023)	1.011	1.007 (1.013)
NCC	105.3	110.7 (110.5)	106.4	108.3 (108.7)
CNC	114.7	102.6 (102.9)	110.3	108.1 (107.9)
NCN	99.9	113.1 (112.3)	106.7	103.5 (103.9)
HNC:	121.1	117.9 (119.1)	124.1	118.4 (118.2)
HNC═	124.1	115.0 (115.9)	125.6	119.6 (118.9)
HC═C═	130.8	128.4 (128.5)	131.0	129.4 (129.3)
HC═N	123.9	120.8 (120.7)	122.7	122.1 (122.1)
HC:N			126.7	117.2 (117.0)

parameter	**5**	**6**	**7**	**8**
:C−N	1.523	1.468	1.348	1.464, 1.464
═C−N	1.425	1.423	1.469	1.472, 1.472
C═C	1.346	1.340	1.528	1.561
═CH	1.086	1.076	1.086(u) 1.092(d)	1.089(u), 1.089(u) 1.087(d), 1.087(d)
:C−H	1.107	1.087(u) 1.105(d)		1.091(u) 1.087(d)
NH	1.019	1.011	1.003	1.015, 1.014
NCC	111.6	109.3	100.3	106.1, 106.0
CNC	105.1	103.4	114.8	102.6, 102.8
NCN	103.7	102.0	104.1	108.4
HNC:	111.0	111.8	120.1	107.2, 107.2
HNC═	108.5	113.1	121.6	108.0, 108.0
HC═C═	126.0	128.6	112.8(u) 111.3(d)	110.2(u), 110.2(u) 113.1(d), 113.0(d)
HC═N	122.4	121.3	112.2(u) 110.9(d)	109.1(u), 109.3(u) 110.4(d), 110.4(d)
HC:N	100.2	111.4(u) 111.1(d)		108.0(u), 108.1(u) 111.7(d), 111.6(d)
HC:H		109.7		108.9
HCH			109.3	107.9, 107.9

[a] Bond distances in Å and bond angles in degrees. Values in parentheses for the radicals are the B3LYP/DZVP2 geometries. For **6**−**8**, (u) and (d) correspond to the H atom being up or down.

TABLE 3: Calculated Harmonic Vibrational Frequencies (cm^{-1}) for Imine 2

mode sym	B3LYP/ DZVP2	MP2/ cc-pVTZ	CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ cc-pVTZ[46]	expt[62]
a′	3467	3482	3405	3440	3263
a′	3154	3197	3159	3152	3024
a′	3047	3090	3049	3052	2914
a′	1702	1679	1651	1675	1638
a′	1480	1494	1464	1483	1452
a′	1361	1378	1371	1387	1344
a′	1070	1074	1063	1073	1058
a"	1154	1178	1141	1162	1127
a"	1086	1100	1056	1080	1061

TABLE 4: Calculated Harmonic Vibrational Frequencies for the Carbenes and Associated Molecules (cm^{-1})

	1		^{3}**1**		**3**		**4**
sym	*ω*	sym	*ω*	sym	*ω*	sym	*ω*
b_1	603	a′	291	a_2	632	a′	354
a_2	624	a″	416	b_1	641	a′	473
a_2	695	a′	614	a_2	706	a″	502
b_1	708	a″	671	b_1	746	a′	574
b_1	756	a′	710	b_1	770	a″	683
a_2	803	a″	813	b_1	853	a′	798
a_1	916	a′	835	a_2	886	a″	850
b_2	921	a″	869	b_2	912	a″	889
b_2	1065	a″	1030	a_1	934	a″	898
a_1	1092	a′	1045	b_2	1084	a′	1000
a_1	1147	a′	1083	a_1	1116	a′	1045
a_1	1176	a′	1146	a_1	1155	a′	1125
b_2	1230	a″	1185	b_2	1205	a″	1141
b_2	1388	a′	1316	a_1	1218	a″	1146
b_2	1411	a″	1320	b_2	1356	a″	1265
a_1	1427	a″	1347	a_1	1464	a″	1358
a_1	1595	a′	1619	b_2	1486	a′	1397
b_2	3307	a″	3253	b_2	1587	a′	1405
a_1	3329	a′	3277	a_1	1613	a′	1635
b_2	3698	a′	3395	b_2	3331	a″	3093
a_1	3698	a″	3399	a_1	3325	a′	3278
				a_1	3338	a″	3301
				b_2	3621	a′	3599
				a_1	3628	a″	3604

	5		**6**		**7**		**8**
sym	*ω*	sym	*ω*	sym	*ω*	sym	*ω*
a′	326	a′	254	a	178	a	92
a"	369	a″	526	b	360	a	331
a′	666	a′	601	a	546	a	672
a′	685	a′	704	b	641	a	717
a″	762	a″	716	b	696	a	807
a′	776	a″	819	a	879	a	840
a″	781	a″	876	b	902	a	886
a″	837	a′	916	a	969	a	931
a″	877	a′	984	b	987	a	943
a′	885	a″	1014	a	1043	a	981
a″	1056	a′	1106	a	1129	a	1072
a′	1065	a″	1121	a	1188	a	1074
a′	1113	a′	1143	b	1198	a	1095
a′	1162	a′	1147	a	1245	a	1102
a″	1264	a″	1229	b	1262	a	1230
a′	1307	a″	1293	a	1337	a	1300
a″	1345	a″	1366	b	1343	a	1316
a″	1423	a′	1414	b	1450	a	1320
a′	1615	a″	1466	a	1498	a	1335
a′	2864	a′	1542	b	1524	a	1373
a″	3144	a′	1662	a	1538	a	1450
a′	3177	a′	2921	a	3075	a	1470
a′	3410	a′	3140	b	3076	a	1510
a″	3424	a″	3282	a	3157	a	1514
		a′	3308	b	3168	a	1529
		a′	3585	b	3702	a	3084
		a″	3585	a	3706	a	3094
						a	3104
						a	3149
						a	3168
						a	3170
						a	3530
						a	3533

The largest errors were found for the CH and NH stretches. Previously, we have found that averaging the CCSD(T)/aug-cc-pVDZ frequencies with the experimental values provides a good estimate of the zero point energy.[35] This yields 24.46 kcal/mol in quite good agreement with the value of 24.69 kcal/mol found by Martin and co-workers[46] using the CCSD(T)/cc-pVTZ quartic force field. We then developed a set of scale factors for the MP2/cc-pVTZ frequencies for **2** to scale them to the average of the CCSD(T)/aug-cc-pVDZ frequencies and the experimental values. The scale factors thus derived are 0.957 for the NH stretch, 0.966 for the C−H stretch, and 0.982 for all of the remaining modes except for the out of plane modes, for which we obtain 0.962. These scale factors were then used to calculate the zero point energy for the other compounds for which no experimental data is known. We used the 0.982 scale factor for the modes between 2000 and 1000 cm^{-1} and the 0.962 scale factor for modes below 1000 cm^{-1}. The calculations of the radicals ^{3}**1** and **4** led to frequencies that were not reasonable (an extra high energy mode) so we reoptimized the geometries at the B3LYP/DZVP2 level and calculated frequencies at this level. The scale factors, obtained as described above for the B3LYP calculations, are 0.979, 0.983, 0.979, and 0.962 starting from the highest frequency scale factors.

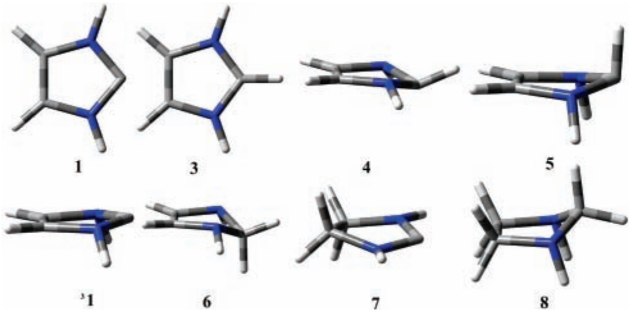

Figure 1. Optimized geometries for **1**−**8**.

The optimized geometries of **1**−**8** exhibit changes in features similar to our earlier calculations and X-ray structures of known substituted analogues where they exist. Optimized structures are depicted in Figure 1. The structure of the parent imidazol-2-ylidene **1** reveals the characteristically small N−C−N angle of 99.9° and C−N distances of 1.366 Å at the carbene center and 1.380 Å to the olefin. The C−C distance in **1** is 1.362 Å. Protonation of **1** to form **3** leads to a widening of the N−C−N angle to 106.7° and shortening of the C−N bonds to the former carbene center to 1.335 Å. The C−C bond in **3** is 1.368 Å and the two nonadjacent C−N bonds are 1.372 Å.

As electron density is added to the imidazole ring by addition of a hydrogen atom, a hydride, or H_2, to the carbene center to form **4**, **5**, and **6** respectively, the imidazole ring becomes distinctly nonplanar and the nitrogens pyramidalize. Larger geometric changes are observed for the more reduced species. The addition of a hydrogen atom leads to a folding of the former carbene center 0.277 Å below the plane of the other four ring atoms in **4**. Pyramidalization of the nitrogens occurs in **4** in a syn-fashion and two N−H’s are trans to the added hydrogen atom. The adjacent C−N bonds in **4** lengthen to 1.419 Å and the N−C−N angle opens to 103.5° relative to **1**.

The addition of a hydride to the carbene center of **1** leads to a very distorted geometry for the ring in **5**. The displacements of the hydrogens around the ring occur in the same fashion as for **4**, but the changes are more exaggerated and the nitrogens and former carbene center are more pyramidal. The carbanion (former carbene) center in **5** lies 0.267 Å above the plane of the other ring atoms. The N−C bonds to the carbanion center are quite long at 1.523 Å and the other C−N bonds are also somewhat lengthened to 1.425 Å. The C−C bond in **5** is 1.345 Å and the N−C−N valence angle is 103.7° (similar to the corresponding values in **4**).

Reduction of the carbene center in **1** by H_2 to form imidazoline **6** also results in a folding of the ring structure as observed for **4** and **5**. The former carbene center in **6** is displaced 0.524 Å below the plane of the other four ring atoms. The nitrogens are pyramidalized to an extent comparable to that in **4** and again show a preference for the syn-geometry. The N−C−N valence angle is 102.0° and the aminal C−N bonds are 1.468 Å. The other C−N and C−C bonds in **6** remain close to the values observed for **5**, 1.423 and 1.340 Å, respectively.

The structure of **³1** reveals a ring geometry that is reminiscent of **4** and to a lesser extent of **5**. A smaller degree of ring distortion is observed and the N−C−N angle is widened to 113.1°. This is consistent with the well-established behavior of triplet carbenes that have larger bond angles at the divalent carbon than in the singlet.[63] The carbene center in **³1** lies only 0.05 Å out of the plane of the other ring atoms. The C−N bonds at the carbene center are 1.409 Å, lengthened relative to their values in **1** similar to our earlier model. The enamine C−N bonds are also lengthened to values of 1.419 Å and the C−C bond shortens to 1.346 Å (relative to **1**).

TABLE 5: Calculated Contributions to Imine 2 Atomization Energies in kcal/mol

contribution^{a}	value
$\Delta E_{\mathrm{elec}}(\mathrm{CBS})^{b}$	437.75
$\Delta E_{\mathrm{CV}}{}^{c}$	1.32
$\Delta E_{\mathrm{SR}}{}^{d}$	−0.38
$\Delta E_{\mathrm{SO}}{}^{e}$	−0.08
$\Delta E_{\mathrm{ZPE}}{}^{f}$	−24.46
$\Sigma D_0{}^{g}$	413.8
$\Delta H_f(0K)$	23.6
$\Delta H_f(0K)$ W2^{h}	23.0
$\Delta H_f(298K)$	21.7
$\Delta H_f(298K)$ W2^{h}	21.1
$\Delta H_f(298K)$ expt	26.4 ± 3.2^{i}
	25 ± 3^{j}
	21 ± 4^{k}
	<22 ± 3^{k}

[a] Results are given in kcal/mol. The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated to the complete basis set limit by using eq 1 with aD, aT, aQ. [c] Core/valence corrections were obtained with the CCSD(T)/cc-pwCVTZ basis sets at the optimized geometries. [d] ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian at the CISD/cc-pVTZ level. [e] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Value of 0.08 for C is based on C. Moore’s Tables, ref 59. [f] The zero point energies were obtained by averaging the CCSD(T)/aug-cc-pVDZ frequencies with the experimental values. [g] The theoretical value of $\Sigma D_0(0K)$. [h] Reference 46. [i] DeFrees, D. J.; Hehre, W. J. *J. Phys. Chem.* **1978**, *82*, 391. [j] Grela, M. A.; Colussi, A. J. *Int. J. Chem. Kinet.* **1988**, *20*, 733. [k] Reference 64.

The imidazolin-2-ylidene **7** shows a geometry in which a twisting of 22.0° has occurred about the saturated C−C bond. The C−N bonds at the carbene center (1.348 Å) are slightly shorter than those for **1**. The N−C−N angle of 104.2° is larger than that in **1** and is characteristic of such “saturated” imidazolin-2-ylidenes.

Full saturation of **7** affords the imidazolidine **8**. There is only a slight twist (0.6°) about the C−C bond so that four of the ring atoms are nearly planar with the unique aminal carbon rising 0.526 Å above the best plane of the other four atoms. The C−N bond distances of 1.464 Å at the aminal center and 1.472 Å at the C_2H_4 unit are consistent with single-bonded, approximately sp^3 centers in the ring. The C−C bond distance is 1.561 Å and the N−C−N angle is 108.4°.

The total atomization energy and its components are given in Table 5 for **2** and in Table 6 for the remaining molecules. The $\Delta H_f(0K)$ values were converted to 298 K following the procedure of Curtiss et al.[44] and are given in Table 7 except for that of **2**, which is given in Table 5. The calculated value of 23.6 kcal/mol for $\Delta H_f(0K)$ of **2** is in quite good agreement with the W2 value of 23.0 kcal/mol.[46] The difference of 0.6 kcal/mol are due to a number of small differences on the order of 0.2 kcal/mol for the zero point energy, $\Delta E_{\mathrm{elec}}(\mathrm{CBS})$, and ΔE_{CV}. Our value confirms the W2 value and is in good agreement with the best estimated value of 21 ± 4 kcal/mol value of Holmes et al.[64] This result together with our previous calculations for C_2H_4, CH_2 ($^3B_1$ and $^1A_1$), and NH_3 suggest that our approach for calculating the heat of formation of **1** should be good to ±1 kcal/mol. We note that use of the CCSD(T)/aug-cc-pVDZ optimized geometry gives a heat of formation that is 0.5 kcal/mol higher than that obtained by using the MP2/cc-pVTZ optimized geometry.

As shown in Table 6, the ΔE_{CV} corrections excluding the ions are ∼4.0 ± 0.3 kcal/mol. The ΔE_{SR} values are all about

TABLE 6: Calculated Energetic Contributions to the Molecular Dissociation Energies Based on CCSD(T)/CBS 0 K Atomization Energies[a]

molecule	CCSD(T)/CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0(0K)[g]
1	922.38	43.73	3.93	−1.15	−0.24	881.19
^{3}**1**	834.15	41.34	3.78	−1.23	−0.24	795.12
3	865.93	52.07	4.27	−1.21	−0.24	816.68
4	962.78	49.42	4.11	−1.24	−0.24	915.99
5	952.83	47.51	3.55	−1.18	−0.24	907.45
6	1052.90	57.80	3.99	−1.15	−0.24	997.70
7	1047.49	57.91	3.85	−1.20	−0.24	991.99
8	1196.52	73.07	3.87	−1.24	−0.24	1,125.84

[a] Results are given in kcal/mol. The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated to the complete basis set limit by using eq 1 with aD, aT, and aQ. [c] The zero point energies were obtained as described in the text. [d] Core/valence corrections were obtained with the CCSD(T)/cc-pwCVTZ basis sets at the optimized geometries. [e] The scalar relativistic correction is the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian at the CISD/cc-PVTZ level. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Value of 0.08 for C is based on C. Moore's Tables, ref 59. [g] The theoretical value of the total dissociation energy ΣD_0(0K).

TABLE 7: Calculated Heats of Formation at 0 and 298 K (kcal/mol) and Calculated Entropies at 298 K

molecule	ΔH_f(0K)	ΔH_f(298K)	S(298K)
1	60.3	56.4	63.8
^{3}**1**	146.4	142.8	69.4
3	176.5	171.6	63.9
4	77.2	72.7	68.8
5	85.7	81.2	67.6
6	47.1	41.5	67.5
7	52.8	47.4	67.3
8	22.2	14.8	70.4
H_2	0.0	0.0	31.2
H	51.63	52.10	27.4
H^+	365.22	365.69	26.0
H^-	34.24	34.71	26.0

TABLE 8: Hydrogenation Energies (kcal/mol) of Carbenes

reaction	$-\Delta H_{\mathrm{rxn}}$(298K)
1 + $H_2 \rightarrow$ **6**	14.9
7 + $H_2 \rightarrow$ **8**	32.6
$^{1}CF_2 + H_2 \rightarrow CF_2H_2$	62.2
^{3}**1** + $H_2 \rightarrow$ **6**	101.3
$^{3}CF_2 + H_2 \rightarrow CF_2H_2$	108.2
$^{3}CH_2 + H_2 \rightarrow CH_4$	110.9

1.2 kcal/mol. Our calculated value for ΔH_f of **1** is 60.3 kcal/mol at 0 K and 56.4 kcal/mol at 298 K. Our error analysis suggests that we should be able to calculate this quantity to within ±1 kcal/mol and we estimate our error bar to be ±1.0 kcal/mol. The first excited triplet state is 86.1 kcal/mol above the singlet. We previously calculated this value at the ROHF-(triplet)/TCSCF(singlet) level with a DZP basis set and obtained 79.4 kcal/mol for the electronic energy difference (the current calculated electronic energy difference between the singlet and the triplet is 88.2 kcal/mol).[14] Thus, the earlier calculations at a lower level provided a semiquantitative value for the singlet−triplet splitting.

The calculated proton affinity of the carbene is 250.5 at 298 K. This value is extremely high for such a simple compound with no substituents. The current calculated value is lower than the value of 257.3 kcal/mol calculated previously at the MP2 level,[14] where we noted that the MP2 value was too high by about 8−10 kcal/mol and estimated a proton affinity for the carbene of ∼250 kcal/mol, in excellent agreement with our more accurate model. We note that the MP2/6-31G** and B3LYP/6-31G* values of 262.1[65] and 258.4[66] kcal/mol, respectively, are too high by up to almost 12 kcal/mol, suggesting that one must be careful in directly calculating accurate proton affinities of these types of carbenes with lower level methods. The CBS-QB3[67] value[68] is 250.2 kcal/mol at 298 K in good agreement with our higher level value.

The ability of the carbene to add an H atom is low with a C−H bond energy of 34.7 kcal/mol at 0 K and 35.8 kcal/mol at 298 K. This can be compared to the ability of CH_2 to add H to form CH_3 with a bond energy of 110.1 kcal/mol at 298 K.[69] This further demonstrates the remarkable stability of the "Arduengo-type" carbene. The ability of the carbene to add H^- is very small, only 8.8 kcal/mol at 0 K, as would be expected due to the excess electron density on the carbene. In fact, **5** is not expected to be stable with respect to loss of an electron as shown by comparing the energies of **4** and **5**.

Addition of H_2 to the carbene is exothermic by 13.2 kcal/mol at 0 K and by 14.9 kcal/mol at 298 K and thus the release of H_2 from **6** is endothermic by the same values. This can be compared to the energy released on adding H_2 to CH_2, which is a much larger 110.9 kcal/mol at 298 K[69] (see Table 8). To see if "Arduengo-type" carbenes can be used for an H_2 storage system, we must also look at the free energy of the reaction. The calculated (and experimental entropies[60] for H, H^+, H^-, and H_2) are given in Table 7. The value of $T\Delta S$ at 298 K is −8.2 kcal/mol and at a likely operating temperature of 80 °C is −9.7 kcal/mol. Although the carbene itself cannot serve as an H_2 storage system because the enthalpy is not favorable enough, substituents can be used to tune this value and substituents are needed to stabilize the carbene against tautomerizations. In addition, application of Le Chatelier's principle suggests that removal of the H_2 by pumping will easily shift the reaction equilibrium and thus enhance the ability of the system to provide dihydrogen. This observation further suggests that pressurizing with H_2 will be useful in regenerating the H_2 storage system. The lower level MP4 calculations[18] give a hydrogenation energy for the carbene of −20.8 kcal/mol without zero point corrections.

The energy to hydrogenate the C═C bond in the carbene to form **7** is −7.5 kcal/mol at 0 K and −9 kcal/mol at 298 K as compared to the value of −32.4 kcal/mol for the hydrogenation of C_2H_4 to C_2H_6 at 298 K.[69] The entropy term for the hydrogenation of the C═C bond in the carbene is −8.3 kcal/mol at 298 K so this would be a reversible storage system at 298 K. Hydrogenation of the saturated carbene at the carbene center is exothermic by 30.6 kcal/mol at 0 K and by 32.6 kcal/mol at 298 K (Table 8). Although this reaction is too exothermic for an H_2 storage system, the hydrogenation energy is still far less than that of CH_2 to form CH_4. The lower level MP4 calculations[18] give a hydrogenation energy for the carbene of −39.7 kcal/mol without zero point corrections.

The hydrogenation energies of the carbenes at the carbene center in Table 8 provide information on the stability of the "Arduengo-type" carbenes. On the basis of the smallest heats of hydrogenation, we would expect that carbenes **1** and **7** are the most stable carbenes as is found experimentally. The fact that the hydrogenation energy for **7** is larger than that of **1** is consistent with the fact that molecules such as **7** are more reactive than molecules based on the framework of **1**. It is clear that CH_2 is unstable on the basis of the large heat released upon hydrogenation. We can also calculate the hydrogenation energy of the triplet state of **1** and its value is comparable to that of CH_2 showing that ^{3}**1** is similar in stability to CH_2. The hydrogenation energy of the carbene CF_2 can be calculated from the available literature data[60,69,70] and it is intermediate between the energies of carbene **1** and CH_2 as would be expected as CF_2 is a singlet carbene that is moderately stable although it cannot be isolated and stored under normal conditions. We note that the hydrogenation energy of $^3CF_2$ can be estimated[71] to be ~108 kcal/mol, comparable to that of CH_2.

Summary

Heats of formation of a number of compounds based on imidazol(in)-2-ylidenes (carbenes) have been calculated by using a reliable approach based on CCSD(T) and extrapolation to the complete basis set limit. The heats of hydrogenation and dehydrogenation of imidazole-derived molecules related to “Arduengo-type” carbenes indicate that with appropriate substitution these heterocycles should make excellent materials for employment as hydrogen storage media. The heats and free energies of reaction lie in a range where one can anticipate easily reversible reactions through employment of mass action effects. Our approach is to first reliably predict the thermodynamic properties before searching for kinetically accessible paths and appropriate catalysts. We are currently exploring the kinetics for these processes with a combined computational/experimental approach.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set. This material is available free of charge via the Internet at http://pubs.acs.org. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) This name for this general class of carbenes has appeared often in the literature. The namesake author on this article is flattered by its use but is reluctant to use the term in his own publication. For completeness in referencing and indexing it has been included herein.

(2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. E. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(3) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(4) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913.

(5) Arduengo, A. J., III; Snyder, J. P.; Padwa, A.; Stengel, T.; Jockisch, A.; Kim, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 11318.

(6) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. *Monatshe* **2000**, *131*, 251.

(7) Arduengo, A. J., III; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348.

(8) Arduengo, A. J., III; Craig, H. A.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Schmutzler, Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.

(9) Arduengo, A. J., III; Krafczyk, R.; Mahler, W.; Marshall, W. J.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1813.

(10) Arduengo, A. J., III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375.

(11) Arduengo, A. J., III; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1963.

(12) Arduengo, A. J., III; Davidson, F.; Goerlich, J. R.; Khasnis, D.; Prakasha, T. K.; Marshall, W. J. *J. Am. Chem. Soc.* **1997**, *119*, 12742.

(13) Arduengo, A. J., III; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *J. Chem. Soc., Chem. Commun.* **1997**, 981.

(14) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180.

(15) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

(16) Arduengo, A. J., III; Bock, H.; Chen, H.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641.

(17) Arduengo, A. J., III; Dixon, D. A.; Kumashiro, K. K.; Lee, C.; Power, W. P.; Zilm, K. W. *J. Am. Chem. Soc.* **1994**, *116*, 6361.

(18) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.

(19) Heinemann, C.; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023.

(20) Su, M.-D.; Chu, S.-Y. *Chem. Phys. Lett.* **1999**, *308*, 283. Su, M.-D.; Chu, S.-Y. *Inorg. Chem.* **1999**, *38*, 4819.

(21) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976.

(22) Schoeller, W. W.; Eisner, D.; Grigoleit, S.; Rozhenko, A. B.; Alijah, A. *J. Am. Chem. Soc.* **2000**, *122*, 10115.

(23) Cheng, M.-J.; Hu, C.-H. *Chem. Phys. Lett.* **2001**, *349*, 477.

(24) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717.

(25) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129.

(26) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449.

(27) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154.

(28) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209.

(29) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384.

(30) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413.

(31) Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373.

(32) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048.

(33) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485.

(34) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576.

(35) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484.

(36) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744.

(37) Ruscic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1.

(38) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727.

(39) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

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

(41) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

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

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

(44) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *103*, 1063.

(45) Martin, J. M. L.; Lee, T. J.; Scuseria, G. E.; Taylor, P. R. *J. Chem. Phys.* **1992**, *97*, 6549.

(46) De Oliveira, G.; Martin, J. M. L.; Silwal, I. K. C.; Liebman, J. F. *J. Comput. Chem.* **2001**, *22*, 1297.

(47) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(48) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R. M.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. MOLPRO-2002, a package of initio programs written by, Universität Stüttgart, Stüttgart, Germany, University of Birmingham, Birmingham, United Kingdom, 2002.

(49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;

Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc., Wallingford CT, 2004.

(50) Apra, E.; Bylaska, E. J.; Jong, W. d.; Hackler, M. T.; Hirata, S.; Pollack, L.; Smith, D.; Straatsma, T. P.; Windus, T. L.; Harrison, R. J.; Nieplocha, J.; Tipparaju, V.; Kumar, M.; Brown, E.; Cisneros, G.; Dupuis, M.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, K.; Valiev, M.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; Lenthe, J. v.; Wong, A.; Zhang, Z. NWChem. PNNL, **2003**. Kendall, R. A.; Aprà, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260−283.

(51) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(52) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(53) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(54) Rittby, M.; Bartlett, R. J. *J. Phys. Chem*. **1988**, *92*, 3033.

(55) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys*. **1994**, *99*, 5219.

(56) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys*. **1994**, *100*, 7410.

(57) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548. Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(58) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett*. **1981**, *84*, 226.

(59) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra, Volume 1, H to V*; U.S. National Bureau of Standards Circular 467; U.S. Department of Commerce, National Technical Information Service, COM-72-50282; U.S. GPO: Washington, DC, 1949.

(60) Chase, M. W., Jr. NIST-JANAF Tables (4th ed.). *J. Phys. Chem. Ref. Data* Mono. 9, Suppl. 1, **1998**.

(61) Pearson, R.; Lovas, F. *J. Chem. Phys.* **1977**, *66*, 4149.

(62) Duxbury, G.; Le Lerre, M. L. *J. Mol. Spectrosc.* **1982**, *92*, 326. Halonen, L.; Duxbury, G. *J. Chem. Phys.* **1985**, *83*, 2078, 2091. Halonen, L.; Duxbury, G. *Chem. Phys. Lett.* **1985**, *118*, 246. Duxbury, G.; Kato, H.; Le Lerre, M. L. *Faraday Discuss.* **1981**, *71*, 97.

(63) Wasserman, E.; Kuck, V. J.; Hutton, R. S.; Yager, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 7491. Herzberg, G. *J. Chem. Phys.* **1971**, *54*, 2276.

(64) Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *Chem. Phys. Lett.* **1992**, *198*, 211.

(65) Sauers, R. R. *Tetrahedron Lett*. **1996**, *37*, 149.

(66) Alder, R. W.; Blake, M. E.; Oliva, J. M. *J. Phys. Chem. A* **1999**, *103*, 11200.

(67) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822. Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(68) Magill, A. A.; Yates, B. F. *Aust. J. Chem.* **2004**, *57*, 1205.

(69) Sander, S. P.; Friedl, R. R.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Molina, M. J.; Moortgat, G. K.; Finlayson-Pitts, B. J. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 14. JPL Publication 02-25; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA, 2003; http://jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_rev02.pdf.

(70) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744.

(71) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54.