

# Atom Equivalents for Relating *Ab Initio* Energies to Enthalpies of Formation.

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Sets of atom equivalents have been developed which permit the estimation of heats of formation,  $\Delta H_f^{\circ 298}(g)$ , from *ab initio* total energies (3-21G and 6-31G\* basis sets). This extends the isodesmic reaction scheme of Pople and the group equivalents of Wiberg. A variety of small inorganic and organic molecules, including fluorocarbons, free radicals, carbocations, and protonated species give excellent agreement with experiment; average errors are less than 1 kcal/mol with unstrained hydrocarbons (both basis sets), and are on the order of 2 kcal/mol for all molecules considered (6-31G\*; the 3-21G basis errors, as expected, usually are somewhat higher). The results substantiate Pople's early conclusions that Hartree-Fock theory provides a generally satisfactory description of classical molecules.

## INTRODUCTION

An impressively large and rapidly increasing set of *ab initio* data for a wide variety of molecules<sup>1,2</sup> gives the chemist an unprecedented opportunity to evaluate the energies of many species for which no experimental values are available. For this purpose, the standardized theoretical models introduced by Pople and his collaborators<sup>2,3</sup> are the most useful, since, by far, the largest amount of mutually consistent data has been collected at such levels.<sup>1</sup> The STO-3G minimal basis set has now been largely replaced by the efficient split-valence basis, 3-21G.<sup>3</sup> Much data is now also accumulating at the 6-31G\* level,<sup>3</sup> a polarization basis set which performs better, *inter alia*, for strained ring systems.<sup>2,3b</sup> Data at correlated levels [e.g., using second order Møller-Plesset perturbation theory (MP2),<sup>3</sup>] are not yet available for very many molecules, but this situation should improve rapidly in the future. The chemist would like a simple way to relate such *ab initio* to experimental energies.

Pople and his collaborators have used isodesmic reactions for this purpose.<sup>2,4</sup> These

formal equations lead to cancellation of errors by maintaining a constant number of different kinds of bonds on both sides of the equation. The energies of such isodesmic reactions often compare very well with experimental values.<sup>2,4</sup> Hence, they can be used with confidence in similar situations to derive heats of formation for molecules where the experimental values are unknown. Even greater precision can be achieved by selecting molecules which have the same number of different kinds of bonds (e.g., C(sp<sup>3</sup>)—H, C(sp<sup>2</sup>)—H, etc.) on both sides of the equation.<sup>5</sup> However, in order to use these approaches, three out of four of the components of the equation must have experimental values. These are not always available. Hence, relatively few heats of formation have been estimated to date from *ab initio* data.

Wiberg<sup>6</sup> and Dewar<sup>7</sup> have recently proposed alternative schemes for deriving heats of formation. Wiberg derived a set of group equivalents (i.e., for CH<sub>3</sub>, CH<sub>2</sub>, CH, and C groups in various environments), and showed them to be very effective in calculating heats of formation of hydrocarbons. Using 6-31G\* data, the RMS error was only about 1 kcal/mol compared to experiment. This is on the order of the experimental uncertainties so that better agreement can hardly

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be achieved. Wiberg's approach is very simple, and can be illustrated for ethane, which consists of two methyl groups. The 6-31G\* energy of ethane is corrected with the experimental heat of formation ( $-20.2$  kcal/mol or  $.03219$  a.u.). This corrected value, divided by 2, gives a group equivalent for  $\text{CH}_3$ . Wiberg's other group equivalents were derived similarly as the averages of larger sets of molecules. With this exception, the resulting scheme is equivalent to the revised<sup>5</sup> Pople isodesmic approach.<sup>2,4</sup>

Dewar's atom equivalent scheme is even simpler.<sup>7</sup> The objective is somewhat different and broader, but the results are less accurate. Dewar chose a much wider set of molecules than Wiberg's hydrocarbons, and assigned a single-atom equivalent value to oxygen and nitrogen as well as to carbon and hydrogen. The average error from experimental heats of formation in the set calculated by Dewar was on the order of 6 kcal/mol for both the 3-21G and 6-31G\* basis sets. Dewar called attention to the equally good performance of MNDO, which gives  $\Delta H^\circ_f$  values directly but is more highly parameterized for this purpose. The virtue of Dewar's approach is its generality: the heats of formation of any species — transition structures, reactive intermediates, non-classical structures, etc. — can be estimated in this manner. However, such "nonclassical" species are generally not described well by Hartree-Fock theory and correlated data will be needed to improve reliability or agreement with experiment.

However, Wiberg's results indicate that much greater accuracy should be achievable with a more flexible approach which includes more parameters than Dewar employed, but is limited to "classical" molecules. A single value for each atom is insufficient, since bonds of a given atom to different neighbors do not have the same energies. We have examined a scheme which in effect is equivalent to Wiberg's<sup>6</sup> and Pople's,<sup>2,4,5</sup> but have assigned separate values to atoms in different environments.

Early work of Pople<sup>4</sup> indicated that Hartree-Fock theory should perform well for classical molecules comprised essentially of two center-two electron bonds. The present results, extending those of Wiberg, allow an updated evaluation of the accuracy achievable with presently available data.

## DERIVATION OF ATOM EQUIVALENTS

The atom equivalents listed in Table I were derived in a consistent way and include values for H, C, N, O, and F in various environments. For each equivalent, averages over as large a set of molecules as possible were taken. The molecules chosen for this purpose were considered to have reliable heats of formation. In a few instances, only a single compound could be employed to derive the atom equivalent (e.g., for  $\text{H}-(\text{H})$  in  $\text{H}_2$ ). Except for  $\text{H}_3^+$ , hydrogen is not attached to hydrogen in other conventional compounds. Such instances are not taken into account in evaluating the overall performance of this procedure.

The notation used in Table I is that of Benson,<sup>8</sup> but it should be noted that our work refers to atom equivalents whereas Benson's tables evaluate data for groups. The number of parameters listed in Table I is rather large, but it can be noted that many values for a given atom are the same or nearly so. This has already been found by Wiberg, and the close correspondence of his group equivalents with those derived from our data is indicated in Table II. Since our interests include reactive intermediates, we have derived atom equivalents calculation of heats of formations of radicals and cations. The latter also permit the estimation of proton affinities for which a substantial body of gas phase data is available in the literature.

The vast majority of *ab initio* data employed (Tables IV–X) were taken from Pople's Archive.<sup>1</sup> With rare exceptions, data always refer to geometries optimized at the same level (i.e., 3-21G//3-21G and 6-31G\*//6-31G\*). This is an improvement, in a few cases, over data used by Wiberg<sup>6</sup> which referred to using single-point calculations carried out at lower-level geometries. Note that some experimentally estimated heats of formation may not be accurate; sometimes more than one value is available. We have given the source of such data in the tables, especially when not included in the more general compilations.<sup>9–12</sup>

*Ab initio* energies refer to a single conformation of a given molecule in the vibrationless state. Most experimental heats of formation are available only at 298 K, and may refer to molecules which exist at that

temperature as a Boltzmann distribution of different conformational isomers with somewhat different energies (e.g., *gauche* and *trans*-butane). Although *ab initio* data can be corrected for zero-point energies,<sup>2</sup> for conversion from 0–298 K,<sup>2</sup> and for the presence of conformers,<sup>13</sup> these quantities are often not available. It is known that these corrections can be included in the energy equivalents with little loss in overall accuracy.<sup>2,4–6</sup> Similarly, correlation energy corrections, which may be very important in other situations, also tend to cancel in comparisons involving classical molecules. In effect, the atom equivalents are parameterized to reproduce experimental  $\Delta H_f^{\circ 298}(g)$  values. The general level of performance of such equivalents provides a test of the self-consistency of *ab initio* theory at the basis set levels examined.

### Atom Equivalents

The atom equivalents at the 3-21G and the 6-31G\* basis set levels are listed in Table I. The units are in hartrees. Benson's convention<sup>8</sup> is used in Table I to designate the atom(s) bonded to the central atom and the type of bonds. For example, the atom equivalent  $C_t-(C_t)(H)$  is used for a triple-bonded carbon atom when it is bound to a hydrogen atom and one other triple-bonded carbon atom (e.g., carbons in a terminal acetylene). With both basis sets, hydrogen was assigned five different atom equivalents according to the atom (H, C, N, O, or F) to which it is bound. These five equivalents are used in all neutral hydrogen-containing molecules. However, in protonated species, additional equivalents for hydrogen are needed, five with the 3-21G and four with the 6-31G\* basis sets. At the 3-21G basis set level, two equivalents are necessary for 0-protonated species: one equivalent for protonated aldehydes and ketones,  $H^+-(O_s)$ . At the 6-31G\* basis set level, both these equivalents merge into one.

Several atom equivalents have been assigned for different types of carbon atoms according to their class, hybridization, and bonded atoms. With the exception of methane and the reactive intermediates, each carbon atom in all hydrocarbons can be classified as saturated, olefinic, or acetylenic. Four equivalents are necessary for the primary, secondary, tertiary, and quaternary saturated carbon atoms:  $C-(C)(H)_3$ ,  $C-(C)_2(H)_2$ ,

$C-(C)_3(H)$  and  $C-(C)_4$ , respectively. Three equivalents,  $C_d-(C_d)(H)_2$ ,  $C_d-(C_d)(C)(H)$  and  $C_d-(C_d)(C)_2$ , are required for different classes of olefinic carbons. The acetylenic carbon can either be terminal or internal. Each type requires its equivalent,  $C_t-(C_t)(H)$  and  $C_t-(C_t)(C)$ , respectively. In the other classes of organic compounds, carbon bound to hetero atom(s) are generally given separate equivalents (fluorocarbons are an exception, see below).

Each type of carbon atoms has been assigned its own equivalent. (The quaternary carbon atom has been excluded at this time since the *ab initio* total energy is only available for neopentane; an equivalent derived from single compound may not be reliable for general use). However, at the 3-21G basis set level, the  $C-(C)_3(H)$  and  $C_d-(C_d)(C)(H)$  equivalents are essentially identical, while the equivalents  $C-(C)_3(H)$ ,  $C_d-(C_d)(C)_2$ ,  $C_t-(C_t)(H)$  and  $C_t-(C_t)(C)$  have the same value at the 6-31G\* basis set level. With both basic sets, the equivalent for the central carbon in an allene,  $C_d-(C_d)_2$ , is the same as the acetylenic carbon equivalent; both are *sp* hybridized. The  $C-(C)(H)_3$  equivalent is used for the methane carbon and the carbon bound to oxygen and/or nitrogen. In each of the basis sets, 3-21G and 6-31G\*, two additional carbon equivalents each are necessary to transform the *ab initio* total energies of carbocations and of free radicals into heats of formation. One equivalent for the carbon carries the positive charge ( $C^+$ ) or the odd electron ( $C^\cdot$ ) and the others,  $C-(C^+)$  and  $C-(C^\cdot)$ , are used for the attached carbon(s).

The nitrogen atoms in amines, amides, imides, nitriles, nitrates, nitrites, imines, diazomethane, and methylhydrazine have different environments. Nevertheless, with both basis sets, the nitrogen atom equivalents in 1°- and 2°-amines as well as methyl hydrazine are the same as the nitrogen equivalent in ammonia. At the 6-31G\* basis set levels, the nitrogen equivalents in amides and imides also have the same value as ammonia. In each basis set, the equivalents  $N_t-(C_t)$ ,  $N-(O_s)(O_d)(C)$ ,  $N-(O_s)(O_d)$ ,  $N_d-(C_d)(H)$ ,  $N_d-(C_d)(N_d)$ , and  $N_d-(N_d)$  are used in nitriles, nitrates, nitrites, imines, and diazomethane. No nitrogen equivalent has been assigned for the nitroso compounds, since the experimental heats of formation of such com-

pounds are not well established. The remaining nitrogen equivalents, Table I, are used for the nitrogen atoms in different nitrogen containing inorganic compounds.

For both basis sets, the oxygen equivalents for water and for oxygen-containing organic molecules such as alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, amides, and imides can be represented adequately by two equivalents. These can also be employed in oxygen-containing inorganic molecules with the exception of oxygen, ozone, and peroxides. These require separate equivalents,  $O_d - (O_d)$ ,  $O_d - (O_d)_2$  and  $O_s - (O_s)(H)$ .

The fluorine atom has been assigned only one equivalent in different fluorides. Geminal and polysubstituted fluorine compounds can be treated in a simple way. Each fluorine atom is considered as if it were carbon. For example, the carbon equivalent in  $CH_2F_2$  is taken to be  $C - (C)_2(H)_2$ . This obviates the need to define  $C - (F)_2(H)_2$  and similar parameters. The  $F - (F)$  equivalent only is used in  $F_2$ .

### Method of Calculation

The transformation of the *ab initio* total energy for a given compound into its heat of formation can be clarified by the following example. To calculate the heat of formation of methanol at the 3-21G basis set level, the sum of the 3-21G equivalents for  $C - (C)(H)_3$ ,  $H - (O)$  and for three  $H - (C)$  (Table I) is subtracted from the 3-21G total energy of methanol. The result is the heat of formation of methanol in hartrees (multiplication by 627.5 gives kcal/mol).

### RESULTS AND DISCUSSION

The Wiberg group equivalents<sup>6</sup> and these derived from the hydrogen and carbon equivalents at the 6-31G\* basis set level are compared in Table II. Since there is no significant difference between the two sets, the atom equivalents for hydrocarbons at the 6-31G\* basis set level perform as well as the Wiberg group equivalents for the estimation of heats of formation.

The available *ab initio* total energies of some hydrocarbons (3-21G and 6-31G\* basis sets) and their experimental heats of formation,  $\Delta H^{298}_{f(g)}$ , are listed in Table III.

**Table I.** Atom equivalents at the 3-21G and 6-31G\* basis set levels.<sup>a</sup>

Atom	Atom equivalents	
	3-21G	6-31G*
H-(H)	-0.56148	-0.56342
H-(C)	-0.56654	-0.56967
H-(N)	-0.56322	-0.56636
H-(O)	-0.55574	-0.56093
H-(F)	-0.53483	-0.56077
H <sup>+</sup> -(H)	-0.56782	-0.56644
H <sup>+</sup> -(C)	-0.55766	-0.56644
H <sup>+</sup> -(N)	-0.62037	-0.60524
H <sup>+</sup> -(O <sub>s</sub> )	-0.62037	-0.59664
H <sup>+</sup> -(O <sub>d</sub> )	-0.60278	-0.59664
H <sup>+</sup> -(F)	-0.60678	-0.59140
C <sub>2</sub> -(H) <sub>3</sub> C	-37.68096 <sup>b</sup>	-37.88935 <sup>b</sup>
C-(H) <sub>2</sub> (C) <sub>2</sub>	-37.67842	-37.88750
C-(H)(C) <sub>3</sub>	-37.67300	-37.88371
C <sub>d</sub> -(H) <sub>2</sub> (C <sub>d</sub> )	-37.67762	-37.88607
C <sub>d</sub> -(H)(C <sub>d</sub> )(C)	-37.67300	-37.88406
C <sub>d</sub> -(C <sub>d</sub> )(C) <sub>2</sub>	-37.66998	-37.88371
C <sub>d</sub> -(C <sub>d</sub> ) <sub>2</sub>	-37.67450	-37.88371
C <sub>t</sub> -(H)(C <sub>t</sub> )	-37.67450	-37.88371
C <sub>t</sub> -(C <sub>t</sub> )(C)	-37.67450	-37.88371
C <sub>a11</sub>	-37.69489	-37.90364
C <sub>a11</sub> -(C <sub>a11</sub> )	-37.67806	-37.88712
C <sub>a11</sub>	-37.71321	-37.92884
C <sub>a11</sub> -(C <sup>+</sup> )	-37.67523	-37.88352
N-(H) <sub>3</sub>	-54.16469	-54.46869
N-(H) <sub>2</sub> C	-54.16469	-54.46869
N-(H)(C) <sub>2</sub>	-54.16469	-54.46869
N-(H)(C)(N)	-54.16469	-54.46869
N-(H) <sub>2</sub> (N)	-54.16469	-54.46869
N-(H) <sub>2</sub> (CO)	-54.17266	-54.46869
N-(H) <sub>2</sub> (O <sub>s</sub> )	-54.17603	-54.47108
N <sub>d</sub> -(H)(C <sub>d</sub> )	-54.13350	-54.45209
N <sub>d</sub> -(H)(N <sub>d</sub> )	-54.15345	-54.47108
N <sub>d</sub> -(C <sub>d</sub> )(N <sub>d</sub> )	-54.13350	-54.45209
N <sub>d</sub> -(N <sub>d</sub> )	-54.13350	-54.45209
N <sub>d</sub> -(N <sub>d</sub> ) <sub>2</sub>	-54.13828	-54.46202
N <sub>d</sub> -(H)(O <sub>d</sub> )	-54.16604	-54.46202
N <sub>d</sub> -(N <sub>d</sub> )(O <sub>d</sub> )	-54.13828	-54.46202
N <sub>d</sub> -(C)(O <sub>d</sub> )(O <sub>s</sub> )	-54.09780	-54.44017
N <sub>d</sub> -(O <sub>d</sub> )(O <sub>s</sub> )	-54.13350	-54.45209
N <sub>t</sub> -(C <sub>t</sub> )	-54.16070	-54.47074
N <sub>t</sub> -(N <sub>t</sub> )	-54.15048	-54.47074
O <sub>s</sub> -(H) <sub>2</sub>	-74.38389	-74.79848
O <sub>s</sub> -(H)(C)	-74.38389	-74.79848
O <sub>s</sub> -(C) <sub>2</sub>	-74.38389	-74.79848
O <sub>s</sub> -(H)(N)	-74.38389	-74.79848
O <sub>s</sub> -(C)(N)	-74.38389	-74.79848
O <sub>s</sub> -(N)	-74.38389	-74.79848
O <sub>s</sub> -(H)(O <sub>s</sub> )	-74.39119	-74.79644
O <sub>d</sub> -(C)	-74.36505	-74.79644
O <sub>d</sub> -(N)	-74.36505	-74.79644
O <sub>d</sub> -(O <sub>d</sub> )	-74.36112	-74.78403
O <sub>d</sub> -(O <sub>d</sub> ) <sub>2</sub>	-74.34791	-74.77198
O <sub>t</sub> -(C)	-74.37054	-74.80671
F-(C)	-98.81559	-99.43989
F-(F)	-98.82212	-99.33888

<sup>a</sup>Benson's<sup>8</sup> convention is used in Table I to indicate the atoms and bonds around the given atom. The subscripts *s*, *d*, and *t* represent the single-bonded, double-bonded, and triple-bonded atom, respectively.

<sup>b</sup>This value is used for methane and carbon bonded to hetero atom(s).

**Table II.** Comparison of the Wiberg group equivalents with those derived from the 6-31G\* equivalents of Table I.

Group	Group equivalents, a.u.	
	Wiberg <sup>6</sup>	Via Table I
CH <sub>3</sub>	-39.59842	-39.59836
CH <sub>2</sub>	-39.02679	-39.02684
CH	-38.45274	-38.45338
=CH <sub>2</sub>	-39.02541	-39.02541
=CH	-38.45321	-38.45373

Columns 6 and 7 give  $\Delta H_f^\circ$  values calculated at the 3-21G and 6-31G\* basis set levels, respectively, by use of the atom equivalents of Table I. The differences between the calculated and the experimental  $\Delta H_f^\circ(g)$ 's are shown in the last two columns of Table III. The good agreement between the experimental and the calculated enthalpies for vari-

ous hydrocarbons at both basis set levels is apparent. In both cases, the average error is about 0.8 kcal/mol (see Table XI for a general summary of the average errors). Hence, the hydrogen and carbon atom equivalents at the 3-21G basis set level are as reliable as the 6-31G\* equivalents.

However, "problem" molecules, aromatic and strained ring hydrocarbons, are not included in Table III. The calculated heats of formation of cyclopropene, cyclopropane, cyclobutene, bicyclobutane, and benzene show that the hydrocarbon atom 3-21G equivalents do not reproduce the experimental enthalpies satisfactorily for all these compounds (Table IV). However, with the exception of benzene, the correlation is reasonably good at the 6-31G\* basis set level, although the errors for the highly strained molecules (e.g., cyclopropene and bicyclobutane) are about 3.7 kcal/mol.

**Table III.** Results of atom equivalent analysis for hydrocarbons.

Mol. Formula	Name	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)^a$ kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
CH <sub>4</sub>	Methane	-39.97688	-40.19517	-17.89	-18.67	-17.03	-0.78	+0.86
C <sub>2</sub> H <sub>2</sub>	Acetylene	-76.39596	-76.81783	54.34	54.04	55.80	-0.30	+1.46
C <sub>2</sub> H <sub>4</sub>	Ethylene	-77.60099	-78.03172	12.45	12.81	11.98	+0.36	-0.47
C <sub>2</sub> H <sub>6</sub>	Ethane	-78.79395	-79.22875	-20.24	-20.58	-20.10	-0.34	+0.14
C <sub>3</sub> H <sub>4</sub>	Propyne	-115.22539	-115.86432	44.39	44.38	44.63	-0.01	+0.24
C <sub>3</sub> H <sub>4</sub>	Allene	-115.21991	-115.86110	45.63	47.68	46.30	+2.05	+0.67
C <sub>3</sub> H <sub>6</sub>	Propene	-116.42401	-117.07147	4.88	4.27	3.78	-0.61	-1.10
C <sub>3</sub> H <sub>8</sub>	Propane	-117.61330	-118.26365	-24.83	-25.50	-25.16	-0.67	-0.33
C <sub>4</sub> H <sub>2</sub>	Dibutylene	-151.65430	-152.49793	113.00	110.93	110.60	-2.07	-2.40
C <sub>4</sub> H <sub>6</sub>	1,3-Butadiene	-154.05946	-154.91960	26.11	25.74	24.27	-0.37	-1.84
C <sub>4</sub> H <sub>6</sub>	2-Butyne	-154.05365	-154.90925	34.71	35.46	34.44	+0.75	-0.27
C <sub>4</sub> H <sub>8</sub>	1-Butene		-156.10499	-0.20		-0.41		-0.21
C <sub>4</sub> H <sub>8</sub>	(Z)-2-Butene		-156.10786	-1.86		-2.31		-0.45
C <sub>4</sub> H <sub>8</sub>	(E)-2-Butene	-155.24637	-156.11041	-2.99	-3.85	-3.91	-0.86	-0.92
C <sub>4</sub> H <sub>8</sub>	Isobutene	-155.24714	-156.11067	-4.26	-3.33	-3.03	+0.93	+1.23
C <sub>4</sub> H <sub>8</sub>	Cyclobutane		-156.09720	6.78		6.38		-0.40
C <sub>4</sub> H <sub>10</sub>	n-Butane	-156.43247	-157.29841 <sup>b</sup>	-30.36	-30.32	-30.13	+0.04	+0.23
C <sub>4</sub> H <sub>10</sub>	Isobutane	-156.43447	-157.29896	-32.41	-33.38	-31.69	-0.97	+0.72
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	-191.71708	-192.79172 <sup>c</sup>	31.94	32.99	31.40	+1.05	-0.54
C <sub>5</sub> H <sub>8</sub>	1,3-Pentadiene	-192.87980		18.12	18.89		+0.77	
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene		-193.94093 <sup>b</sup>	25.25		27.73		+2.48
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	-192.90168	-193.97717	8.23	7.47	6.78	-0.76	-1.45
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	-194.08847	-195.16295	-18.44	-19.43	-18.04	-0.99	+0.40
C <sub>5</sub> H <sub>12</sub>	n-Pentane		-196.33302 <sup>b</sup>	-35.10		-35.00		+0.10
C <sub>6</sub> H <sub>12</sub>	Cyclohexane		-234.20796	-29.50		-29.44		+0.06

<sup>a</sup>The experimental  $\Delta H_f^\circ(g)$  are from Ref. 2.

<sup>b</sup>Ref. 6.

<sup>c</sup>K. B. Wiberg and J. J. Wendoloski, *J. Am. Chem. Soc.* **104**, 5679 (1982).

**Table IV.** Results of atom equivalent analysis for strained hydrocarbons and benzene.

Mol. Formula	Name	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)^a$ kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol		Diff.	
		3-21-G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
C <sub>3</sub> H <sub>4</sub>	Cyclopropene	-115.16201	-115.82305	66.20	80.68	69.81	+14.48	+3.61
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	-116.40121	-117.05887	12.73	20.89	13.59	+8.16	+0.86
C <sub>4</sub> H <sub>6</sub>	Cyclobutene	-154.03072	-154.89962	37.45	44.78	38.60	+7.33	+1.15
C <sub>4</sub> H <sub>6</sub>	Bicyclobutane	-153.98664	-154.87169	51.90	71.44	55.69	+19.54	+3.79
C <sub>6</sub> H <sub>6</sub>	Benzene	-229.41945	-230.70305 <sup>b</sup>	19.81	11.16	12.13	-8.65	-7.68

<sup>a</sup>The experimental  $\Delta H_f^\circ(g)$  are from Ref. 9.<sup>b</sup>Ref. 6.**Table V.** Results of atom equivalent analysis for nitrogen- and oxygen-containing organic compounds.

Mol. Formula	Name	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)^a$ kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
CHN	Hydrogen cyanide	-92.35408	-92.87520	32.3 <sup>b</sup>	33.96	34.24	+1.66	+1.94
CH <sub>5</sub> N	Methyl amine	-94.68166	-95.20983	-5.50	-6.24	-6.31	-0.74	-0.81
CH <sub>2</sub> N <sub>2</sub>	Diazomethane	-146.99582	-147.84320 <sup>c</sup>	55.0 <sup>d</sup>	53.48	56.27		
				46.0 <sup>e</sup>				
				71.0 <sup>f</sup>				
CH <sub>6</sub> N <sub>2</sub>	Methyl hydrazine		-150.20108	22.6 <sup>f</sup>		21.2		-1.4
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	-131.19180	-131.92753	20.9 <sup>e</sup>	19.10	19.4	-1.8	-1.5
C <sub>2</sub> H <sub>3</sub> N	Methyl isocyanide	-131.15917		35.6 <sup>e</sup>	39.58		+3.98	
C <sub>2</sub> H <sub>5</sub> N	Acetaldimine	-132.32300	-133.07384	2.0 <sup>g</sup>	1.13	1.25	-0.87	-0.75
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	-133.50415	-134.24761	-11.35	-11.55	-12.02	-0.20	-0.67
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	-133.49485	-134.23885	-4.43	-3.63	-4.44	+0.80	-0.01
C <sub>2</sub> N <sub>2</sub>	Cyanogen	-183.56292	-184.59122	73.84 <sup>e</sup>	75.55	80.92	+1.71	+7.08
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile	-170.01133		12.10 <sup>e</sup>	14.06		+1.96	
CH <sub>2</sub> O	Formaldehyde	-113.22182	-113.86633	-25.92	-26.81	-25.85	-0.89	+0.07
CH <sub>4</sub> O	Methanol	-114.39802	-115.03542	-48.07	-48.83	-48.72	-0.76	-0.65
CH <sub>2</sub> O <sub>2</sub>	Formic acid	-187.70019	-188.76231	-90.57	-92.88	-92.52	-2.31	-1.95
C <sub>2</sub> H <sub>2</sub> O	Ketene	-150.87653	-151.72467	-11.40 <sup>f</sup>	-12.44	-8.45	-1.04	+2.95
C <sub>2</sub> H <sub>4</sub> O	Acetaldehyde	-152.05525	-152.91596	-39.73	-38.98	-38.99	+0.75	+0.74
C <sub>2</sub> H <sub>6</sub> O	Ethanol	-153.22268	-154.07574	-56.24	-55.49	-56.02	+0.75	+0.22
C <sub>2</sub> H <sub>6</sub> O	Dimethylether	-153.21321	-154.06474	-43.99	-42.77	-43.64	+1.22	+0.35
C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	Glyoxal	-225.30696	-226.59218	-50.66	-51.37	-50.99	-0.71	-0.33
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic Acid	-226.53423		-103.26	-105.43		-2.17	
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	-226.51427		-83.7 <sup>e</sup>	-86.12		-2.42	
C <sub>3</sub> H <sub>4</sub> O	Propenal	-189.68988		-18.0 <sup>h</sup>	-17.0		+1.0	
C <sub>3</sub> H <sub>6</sub> O	Acetone	-190.88722	-191.96225	-51.7 <sup>f</sup>	-50.23	-50.04	+1.47	+1.66
CH <sub>3</sub> NO	Formamide	-167.98490	-168.93070	-44.50 <sup>e</sup>	-45.96	-46.33	-1.46	-1.83
CH <sub>4</sub> N <sub>2</sub> O	Urea	-222.73682	-223.98219	-58.7	-58.1	-58.7	+0.6	0.0
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrate	-242.25585	-243.66198	-17.9 <sup>f</sup>	-17.9	-17.9	0.0	0.0
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	-242.28636	-243.66864	-15.6 <sup>f</sup>	-14.65	-14.6	+0.95	+1.0
C <sub>2</sub> H <sub>5</sub> NO	Acetamide	-206.81594		-57.0 <sup>i</sup>	-56.6		+0.4	
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Ethyl nitrate		-282.70102	-24.38		-24.40		-0.02

<sup>a</sup>The experimental  $\Delta H_f^\circ(g)$  are from Ref. 9 unless otherwise specified.<sup>b</sup>Ref. 8.<sup>c</sup>C. Thomson and C. Glidewell, *J. Comput. Chem.* **4**, 1 (1983).<sup>d</sup>J. Vogt, A. D. Williamson and J. L. Beauchamp, *J. Am. Chem. Soc.* **100**, 3478 (1978).<sup>e</sup>Ref. 11.<sup>f</sup>Ref. 8.<sup>g</sup>M. R. Ellenberger, R. A. Eades, M. W. Thomsen, W. E. Farneth and D. A. Dixon, *J. Am. Chem. Soc.* **101**, 7151 (1979).<sup>h</sup>J. H. Vajda and A. G. Harrison, *Int. J. Mass. Spectrom. Ion Phys.* **30**, 293 (1979).<sup>i</sup>Ref. 10.

These results are in accord with expectations. Basis sets with polarization functions (such as 6-31G\*) are known to be needed to describe the energies of small carbocyclic rings<sup>2,3b</sup> whereas electron correlation corrections are significant in aromatic systems such as benzene, which are stabilized by extensive electron delocalization (resonance).<sup>14</sup>

The heats of formation, experimental and calculated, of nitrogen- and oxygen-containing organic compounds are listed in a similar manner in Table V. The molecules included belong to different classes of organic compounds such as nitriles, amines, imines, diazomethane, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, ketene, amides, and imides. There is good agreement between the experimental and the calculated

enthalpies. The average error (Table XI) is about 1.2 kcal/mol at the 6-31G\* basis set level and the 3-21G basis performs nearly as well (1.3 kcal/mol). However, the relatively large error in the calculated  $\Delta H_f^\circ(g)$  of cyanogen, 7 kcal/mol at the 6-31G\* basis set level, is difficult to understand.

The calculated heats of formation of free radicals and carbocations is compared with experimental data in Tables VI and VII, respectively. The average error for the free radicals is about 1.5 kcal/mol at the 6-31G\* basis set level while it is about 2.2 kcal/mol at the 3-21G basis set level. The second average error is acceptable since the experimental uncertainty (Table VI) is 1–2 kcal/mol for most free radicals.<sup>12</sup> The average errors for carbocations are 2.95 and 3.95 kcal/mol at the

**Table VI.** Results of atom equivalent analysis for free radicals.

Formula	Radical	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)^a$	Calc. $\Delta H_f^\circ(g)$ kcal/mol.		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
CH <sub>3</sub>	Methyl	-39.34261	-39.55899	35.1 $\pm$ 0.15	32.6	33.7	-2.5	-1.4
CH <sub>4</sub> N	Aminomethyl	-94.06305	-94.58673	35.7 $\pm$ 2	35.2	36.2	-0.5	+0.5
C <sub>2</sub> H	Ethynyl	-75.73206	-76.15009	135 $\pm$ 1	130	132	-5	-3
C <sub>2</sub> H <sub>3</sub>	Vinyl	-76.96279	-77.39029	70.4 $\pm$ 2	68.9	68.7	-1.5	-1.7
C <sub>2</sub> H <sub>5</sub>	Ethyl	-78.16364	-78.59715	25.9 $\pm$ 1	26.4	26.3	+0.5	+0.4
C <sub>3</sub> H <sub>7</sub>	n-Propyl	-116.98249	-117.63144	21.0 $\pm$ 1	23.3	22.8	+2.3	+1.8
C <sub>3</sub> H <sub>7</sub>	Isopropyl	-116.98441	-117.63438	18.2 $\pm$ 1	20.3	19.6	+2.1	+1.4
C <sub>4</sub> H <sub>9</sub>	tert-Butyl	-155.80910	-156.67501	8.7 $\pm$ 1	11.8	10.7	+3.1	+2.0

<sup>a</sup> Ref. 12.

**Table VII.** Results of atom equivalent analysis for classical carbocations.

Formula	Carbocation	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)$ kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol.		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
CH <sub>3</sub>	Methyl	-39.00913	-39.23064	261 <sup>a</sup>	253	256	-8	-5
C <sub>2</sub> H <sub>3</sub>	Vinyl	-76.65577	-77.08673	266.9 <sup>b</sup>	271	273	+4.1	+6.1
C <sub>2</sub> H <sub>5</sub>	Ethyl	-77.87260	-78.31123	215.6 <sup>c</sup>	219.0	219.0	+3.4	+3.4
C <sub>3</sub> H <sub>3</sub>	Cyclopropenyl	-114.32957	-115.00702	256 <sup>a</sup>	272	250	+16	-6
C <sub>3</sub> H <sub>3</sub>	Propargyl	-114.30949	-114.95110	281 <sup>a</sup>	284	285	+3	+4
C <sub>3</sub> H <sub>5</sub>	Allylic	-115.54214	-116.19321	225 <sup>c</sup>	224	222	-1	-3
C <sub>3</sub> H <sub>7</sub>	Isopropyl	-116.72620	-117.38076	191 <sup>c</sup>	190	190	-1	-1
C <sub>4</sub> H <sub>9</sub>	sec-Butyl	-155.55311	-156.42081	183 <sup>c</sup>	182	183	-1	0.0
C <sub>4</sub> H <sub>9</sub>	tert-Butyl	-155.57274	-156.44241	166 <sup>c</sup>	166	166	0.0	0.0
C <sub>5</sub> H <sub>9</sub>	Cyclopentyl	-193.212177	-194.29211	191 <sup>d</sup>	193	192	+2	+1

<sup>a</sup> M. T. Bowers, *Gas Phase Ion Chemistry*, Vol. 2 (Academic Press, New York, 1979).

<sup>b</sup> D. D. Wagman, W. H. Evans, V. P. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*, *J. Chem. Ref. Data*, Suppl. No. 2, 11 (1982).

<sup>c</sup> Ref. 11.

<sup>d</sup> N. L. Allinger, H. Dodziuk, D. W. Rogers, and S. N. Naik, *Tetrahedron* 38, 1593 (1982).

**Table VIII.** Results of atom equivalent analysis for fluorinated hydrocarbons.<sup>a</sup>

Mol. Formula	Name	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)$ <sup>a</sup> kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol.		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
CFH <sub>3</sub>	Fluoromethane	-138.28189	-139.03461	-55.9 <sup>b</sup>	-53.8	-54.2	+2.1	+1.7
CF <sub>2</sub> H <sub>2</sub>	Difluoromethane	-236.60910	-237.89635	-107 <sup>b</sup>	-104.4	-106.5	+2.6	+0.5
CF <sub>3</sub> H	Trifluoromethane	-334.95172	-336.77164	-166.3 <sup>c</sup>	-166.5	-168.5	-0.2	-2.2
CF <sub>4</sub>	Tetrafluoromethane	-433.29631		-223.3 <sup>c</sup>	-226.5		-3.2	
C <sub>2</sub> FH <sub>3</sub>	Fluoroethene	-175.92057	-176.88195	-33 <sup>d</sup>	-34.4	-33.2	-1.4	-0.2
C <sub>2</sub> FH <sub>5</sub>	Fluoroethane	-177.10897	-178.07722	-63 <sup>d</sup>	-63.6	-64.1	-0.6	-1.1
C <sub>2</sub> F <sub>2</sub> H <sub>2</sub>	1,1-Difluoroethene	-274.24746	-275.74000	-82.0 <sup>e</sup>	-85.1	-82.3	-3.1	-0.3
C <sub>2</sub> F <sub>2</sub> H <sub>2</sub>	(E)-1,2-Difluoroethene	-274.22911	-275.72173	-70.0 <sup>f</sup>	-74.6	-71.8	-4.6	-1.8
C <sub>2</sub> F <sub>2</sub> H <sub>2</sub>	(Z)-1,2-Difluoroethene	-274.22687	-275.72130		-66.4	-67.3		
C <sub>2</sub> F <sub>4</sub>	Tetrafluoroethene	-470.85535	-473.41567	-157.9 <sup>c</sup>	-158.8	-156.1	-0.9	+1.8
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	-668.74489		-321.3 <sup>c</sup>	-317.1		+4.2	

<sup>a</sup>The fluorine atom is considered as a carbon to classify the carbon to which the fluorine atom(s) is(are) bonded. The quaternary carbon is treated as 3° carbon, e.g., CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>.

<sup>b</sup>Ref. 11.

<sup>c</sup>Refs. 9 and 10.

<sup>d</sup>R. W. Taft, "Gas Phase Proton Transfer Equilibria," in *Proton Transfer Reactions*, E. F. Caldin and V. Gold, Eds., pp. 31-78 (John Wiley & Sons, New York, 1975).

<sup>e</sup>S. A. McLuckey, D. Cameron, and R. G. Cooks, *J. Am. Chem. Soc.* **103**, 1313 (1981).

<sup>f</sup>J. P. Stadelmann and J. Vogt, *Int. J. Mass Spectrom. Ion Phys.* **35**, 83 (1980).

**Table IX.** Results of atom equivalent analysis for small inorganic molecules.

Mol. Formula	Molecule	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)$ <sup>a</sup> kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol.		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
H <sub>2</sub>	Hydrogen	-1.12296	-1.12683	0.0	0.0	0.0	0.0	0.0
H <sub>3</sub> N	Ammonia	-55.87220	-56.18436	-11.0	-11.2	-10.41	-0.20	+0.59
H <sub>2</sub> N <sub>2</sub>	(E)-Diimide	-109.35477	-109.99477	48.7 <sup>±5b</sup> 36.0 <sup>±2c</sup> 50.7 <sup>±2d</sup>	49.3	50.3		
H <sub>2</sub> N <sub>2</sub>	(Z)-Diimide	-109.34240	-109.98350	50 <sup>±5</sup>	57.1	57.3		
H <sub>4</sub> N <sub>2</sub>	Hydrazine	-110.55000	-111.16937	22.8	20.24	20.99	-2.56	-1.81
HN <sub>3</sub>	Hydrogen azide	-162.87642	-163.83870	70.3 <sup>e</sup>	70.3	70.8	0.0	+0.5
H <sub>2</sub> O	Water	-75.58596	-76.01075	-57.8	-56.84	-56.73	+0.95	+1.07
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide	-149.94582	-150.76479	-32.6	-32.6	-31.4	0.0	+1.2
H <sub>2</sub> O <sub>3</sub>	H-O-O-O-H	-224.31182		(-13.5)	-16.8			
HNO (triplet)	H-N=O	-129.05638	-129.78771	23.8	23.8	23.3	0.0	-0.5
H <sub>3</sub> NO	Hydroxylamine	-130.25644	-130.97884	-9.0	-9.0	-9.8	0.0	-0.8
HNO <sub>2</sub> (cis)	Nitrous acid	-203.46850		-18.3 <sup>e</sup>	-19.0		-0.7	
HNO <sub>2</sub> (trans)	Nitrous acid	-203.46601		-18.84	-17.46		+1.38	
HF	Hydrogen fluoride	-99.46022	-100.00291	-64.8	-64.8	-64.8	0.0	0.0
CO	Carbon monoxide	-112.09330	-112.73788	-26.24 <sup>f</sup>	-26.23	-26.24	+0.01	0.0
CO <sub>2</sub>	Carbon dioxide	-186.56126	-187.63418	-94.05 <sup>f</sup>	-94.25	-95.35	-0.20	-1.30
N <sub>2</sub>	Nitrogen	-108.30095	-108.94395	0.0	0.0	-1.55	0.0	-1.55
N <sub>2</sub> O(linear)	Nitrous oxide	-182.60562	-183.68012	19.6 <sup>e</sup>	19.6	19.1	0.0	-0.5
O <sub>2</sub> (singlet)	Oxygen	-148.68718	-149.53300	22.0 <sup>e</sup>	22.0	22.0	0.0	0.0
O <sub>3</sub>	Ozone	-222.98922	-224.26144	34.2 <sup>e</sup>	34.2	34.2	0.0	0.0
F <sub>2</sub>	Fluorine	-197.64424	-198.67776	0.0	0.0	0.0	0.0	0.0

<sup>a</sup>Data are from Ref. 8 unless otherwise specified.

<sup>b</sup>S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **29**, 442 (1958).

<sup>c</sup>C. Willis, F. P. Lossing, and R. A. Back, *Can. J. Chem.* **54**, 1 (1976).

<sup>d</sup>S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **68**, 3162 (1978).

<sup>e</sup>W. Thiel, *J. Am. Chem. Soc.* **103**, 1413 (1981).

<sup>f</sup>Ref. 9 and 10.



**Table X.** Results of atom equivalent analysis for protonated molecules.

Mol. Formula	Protonated Molecule	E(HF), a.u.		Exp. $\Delta H_f^\circ(g)^a$ kcal/mol	Calc. $\Delta H_f^\circ(g)$ kcal/mol.		Diff.	
		3-21G	6-31G*		3-21G	6-31G*	3-21G	6-31G*
H <sub>3</sub> <sup>+</sup>	Hydrogen	-1.27006	-1.27429	264	264	263	0.0	-1
H <sub>4</sub> N <sup>+</sup>	Ammonia	-56.23386	-56.53077	151	151	152	0.0	+1
H <sub>5</sub> N <sub>2</sub> <sup>+</sup>	Hydrazine	-110.91020	-111.51833	184	183.5	181.8	-0.5	-2.2
H <sub>3</sub> O <sup>+</sup> (C <sub>3v</sub> )	Water	-75.89123	-76.28934	141	140.9	142.8	-0.1	+1.8
H <sub>3</sub> O <sub>2</sub> <sup>+</sup> (trans)	Hydrogen peroxide	-150.22819	-151.03296	171	179.5	174.7	+8.5	+3.7
H <sub>4</sub> NO <sup>+</sup>	Hydroxylamine <sup>b</sup>		-131.26158			187.2		
H <sub>4</sub> NO <sup>+</sup>	Hydroxylamine <sup>c</sup>	-130.59075	-131.30677		170.5	164.2		
H <sub>2</sub> F <sup>+</sup>	Hydrogen fluoride	-99.67050	-100.19782	184	184	184	0.0	0.0
<sup>+</sup> CH <sub>5</sub>	Methane	-40.16056	-40.38850	216	216	217	0.0	+1
CH <sub>2</sub> N <sup>+</sup>	Hydrogen cyanide	-92.64558	-93.15904	226.5	240.3	235.9	+13.8	+9.4
CH <sub>2</sub> N <sup>+</sup>	Hydrogen isocyanide	-92.64558	-93.15904	222.5	198.9	209.5	-23.6	-13.0
CH <sub>6</sub> N <sup>+</sup>	Methyl amine	-95.05934	-95.57349	146.	146.	145.3	0.0	-0.7
CH <sub>3</sub> O <sup>+</sup>	Formaldehyde	-113.51414	-114.15643	168.	168.	166.5	0.0	-1.5
CH <sub>5</sub> O <sup>+</sup>	Methanol	-114.72492	-115.33899	135.5	135.3	135.2	-0.2	-0.3

<sup>a</sup> S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data* (in press).<sup>b</sup> O-Protonated hydroxylamine.<sup>c</sup> N-Protonated hydroxylamine.

6-31G\* and the 3-21G basis set levels, respectively. They are higher than those for the free radicals. The reason can be attributed, especially at the 3-21G basis set level, to the large deviation of the calculated from the experimental enthalpy of the cyclopropenyl cation. Here again, the equivalents at the 3-21G basis set level fail to correlate the experimental and the calculated enthalpies in such a strained, aromatic cation. However, the average errors are improved to 2.6 kcal/mol at both basis set levels after excluding the cyclopropenyl cation. This error is still higher than those for free radicals (1.5 and 2.2), but it is acceptable since the experimental range of the enthalpies for carbocations is between 200 and 300 kcal/mol and the experimental values are even less certain.<sup>11</sup>

The error for the vinyl cation (Table VII) is higher than any of saturated cations, but no separate equivalent for C<sup>+</sup> (sp) was employed.

The results for fluorinated hydrocarbons (Table VIII) show a good agreement between the experimental and the calculated enthalpies. The average error at 6-31G\* (1.2 kcal/mol) is better than that at 3-21G (2.3 kcal/mol).

The calculated enthalpies for small inorganic molecules are listed in Table IX. The average 3-21G error is only 0.33 kcal/mol. The average error at the 6-31G\* basis set level (0.61) is about twice as large, but the number of atom equivalents used at 3-21G

**Table XI.** Average errors (kcal/mol) for the entries in Tables III–X.

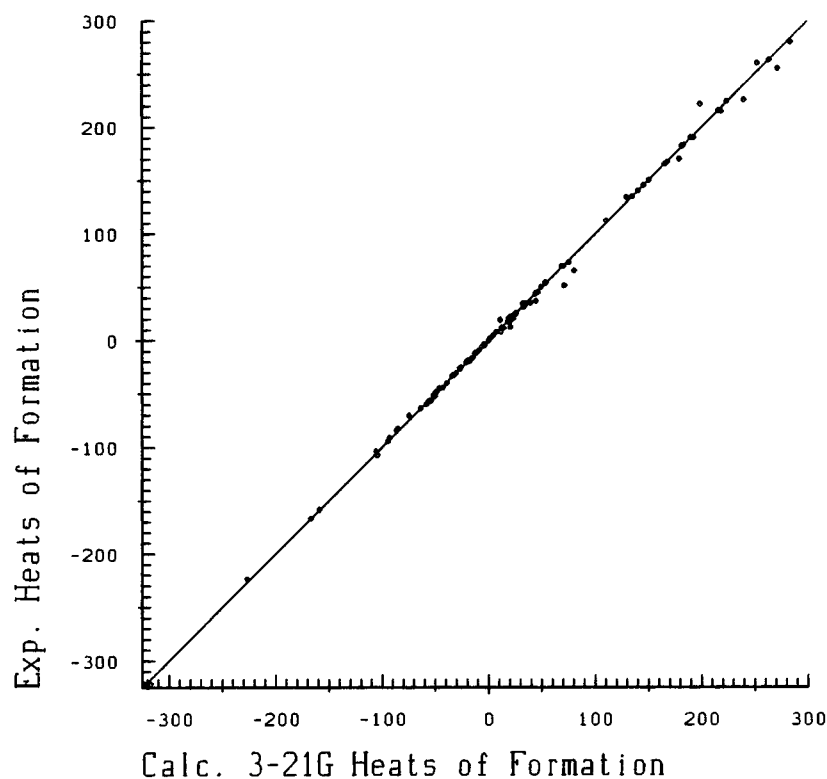
	3-21G	6-31G*
Table 3	0.8	0.8
Table 4	11.6	3.4
Table 5	1.3	1.2
Table 6	2.2	1.5
Table 7	4.0	3.0
Table 8	2.3	1.2
Table 9	0.3	0.6
Table 10	3.9	2.9

is larger than the number employed at the 6-31G\* (e.g., the N<sub>i</sub>—(N<sub>i</sub>) and N<sub>i</sub>—(C<sub>i</sub>) 6-31G\* equivalents have the same value while each one has its own value at 3-21G).

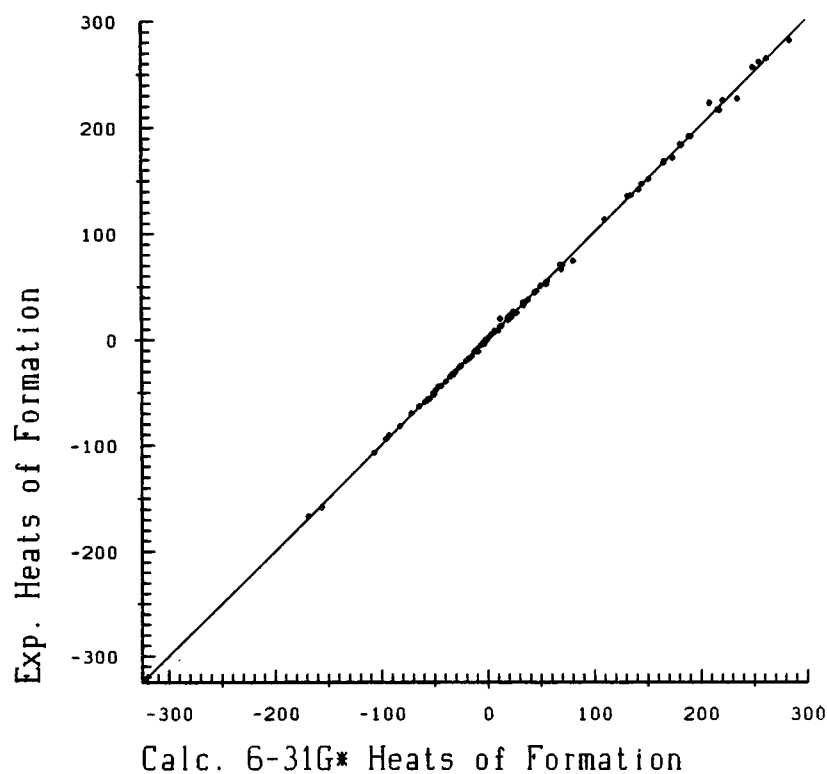
The correlation between the calculated and the experimental enthalpies for the protonated species (Table X) are better at the 6-31G\* than at the 3-21G basis set level (e.g., with hydrogen peroxide, hydrogen cyanide, and isocyanide). The calculated enthalpies for the O- and N-protonated hydroxyl amine are 187.2 and 164.2 kcal/mol at the 6-31G basis set level.

## CONCLUSIONS

As pointed out by Pople many years ago, Hartree-Fock theory provides generally very



**Figure 1.** Plot of experimental  $\Delta H_f^{\circ 298}(g)$  values for the compounds listed in Tables III–X against the  $\Delta H_f^{\circ}$  values calculated by using the 3-21G atom equivalents and 3-21G//3-21G total energies. Slope 1.000 was taken for the correlation line.



**Figure 2.** As in Figure 1, except that 6-31G\*//6-31G\* data and the corresponding atom equivalents were employed. Slope 1.000 was taken for the correlation line.

satisfactory descriptions of classical molecules (i.e., those which can be represented adequately by a single Lewis structure with localized two electron bonds). The success of HF theory with regard to relative energies is demonstrated dramatically by the plots, Figures 1 (3-21G) and 2 (6-31G\*), which include all the data (Tables III–X) analyzed in the present paper.

Hence, the atom equivalents at both basis set levels can be used with confidence for the conversion of *ab initio* total energies into enthalpies of formation for organic compounds, classical saturated carbocations, free radicals, fluorinated hydrocarbons, small inorganic molecules, and protonated species. However, the equivalents at the 3-21G basis set level cannot be used safely for strained molecules. The equivalents at both basis set levels do not give good results for benzene.

In future, data obtained at electron correlated levels will be analyzed similarly. This is expected to extend the treatment to systems which extended electron delocalization, aromatic and electron deficient systems, as well as transition structures.

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