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Benchmark Thermochemistry of the Hydroperoxyl Radical[†]

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A theoretical estimation of the enthalpy of formation for the hydroperoxyl radical is presented. These results are based on CCSD(T)/aug-cc-pCV5Z calculations extrapolated to the basis-set limit with additional corrections. Anharmonic vibrational zero-point energies, scalar relativistic, spin−orbit coupling, and diagonal Born−Oppenheimer corrections are further used to correct the extrapolated term energies, as well as various empirical corrections that account for correlation effects not treated at the CCSD(T) level. We estimate that $\Delta_f H^\circ_0 = 3.66 \pm 0.10$ kcal mol^{-1} ($\Delta_f H^\circ_{298} = 2.96 \pm 0.10$ kcal mol^{-1}) using several reaction schemes. Significantly, it appears to be necessary to include effects of connected pentuple excitations in order to achieve an uncertainty of ca. 0.1 kcal mol^{-1}.

1. Introduction

The hydroperoxyl radical ($HO_2^\bullet$) is a key transient in combustion of hydrocarbon fuels, atmospheric photolysis cycles, and biochemical processes. The branching ratio of $H + O_2 \rightleftharpoons HO_2 \rightleftharpoons OH + O$ is of great importance in hydrocarbon combustion mechanisms, which are strongly tied to the value of $\Delta_f H^\circ_{298}$ (HO_2)[1]. Reactions between hydrogen (HO_x, $x = 1, 2$) and nitrogen oxide species (NO_x, $x = 1, 2$) are believed to be very important in atmospheric chemistry. In the upper troposphere, the reaction $HO_2 + NO \rightarrow OH + NO_2$ and subsequent NO_2 photolysis is thought to regulate ozone production.[2,3] Recently the near-IR photolysis of HOONO has been postulated to account for enhanced levels of HO_x observed during twilight periods.[4,5] To fully understand the ramifications of this channel, the strength of the HOO−NO bond must be known. Clearly, the underlying thermodynamic stability of the hydroperoxyl radical is a quantity that needs to be known precisely and accurately.

However, unlike for many small radicals formed from first- and second-row atoms, the enthalpy of formation of HO_2 has proven difficult to pin down. The JPL compendium[6] lists $\Delta_f H^\circ_{298}$ (HO_2) = 3.3 ± 0.8 kcal mol^{-1}, while the NIST-JANAF thermochemical tables[7] give $\Delta_f H^\circ_{298}$ (HO_2) = 0.5 ± 2.1 kcal mol^{-1}. A review of earlier experimental results was published by Shum and Benson,[8] who determined that $\Delta_f H^\circ_{298}$ (HO_2) = $3.5^{+1.0}_{-0.5}$ kcal mol^{-1} based on early ionization and equilibrium experiments.[9] More recent results have given similar values but have not succeeded in further lowering the uncertainty. By use of a beam of O_2^+ ions, Fisher and Armentrout[10] directly measured the CH_3^+ appearance threshold energy to determine $\Delta_f H^\circ_{298}$ (HO_2) from the reaction $O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2$. From this study, $\Delta_f H^\circ_{298}$ (HO_2) = 3.8 ± 1.2 kcal mol^{-1} was obtained. Another experimental investigation using a similar technique was reported by Holmes et al.[11] By bombardment of *tert*-butyl hydroperoxide with energetic electrons, the C−O bond ruptures to produce hydroperoxyl radical fragments. The formation enthalpy at 298 K of hydroperoxyl from this process was determined to be 3.5 ± 3 kcal mol^{-1}. In 1998, the enthalpy of formation for HO_2 was again investigated with photoionization mass spectrometry (PIMS). Litorja and Ruscic[12] used vacuum ultraviolet photons to dissociate hydrogen peroxide via $H_2O_2 + h\nu \rightarrow HO_2^+ + H + e^-$. By measuring the appearance potential of HO_2^+ and combining that with the known ionization potential of HO_2, the $H-O_2H$ bond dissociation energy (BDE) was determined. The BDE is then used to calculate $\Delta_f H^\circ$ (HO_2) from the relationship

$$\Delta_f H^\circ\,(HO_2) = \mathrm{BDE}\,(HO_2 - H) + \Delta_f H^\circ\,(H_2O_2) - \Delta_f H^\circ\,(H)$$

The results from these elegant experiments were reported to be 4.0 ± 0.8 kcal mol^{-1} at 0 K (3.3 ± 0.8 kcal mol^{-1} at 298 K). The most recent determination of $\Delta_f H^\circ_{298}$ (HO_2) was published in 2002. Raymond et al.[13] used photodetachment spectroscopy and flowing afterglow-selected ion flow tube measurements to extract $\Delta_f H^\circ_{298}$ (HO_2) = 3.2 ± 0.5 kcal mol^{-1} and $\Delta_f H^\circ_0$ (HO_2) = 3.9 ± 0.5 kcal mol^{-1}. Finally, using the active table approach, Ruscic recently estimated that $\Delta_f H^\circ_0$ is 3.76 ± 0.21 kcal mol^{-1}.[14]

In addition to experimental work, ab initio calculations have been used to estimate the thermochemical stability of HO_2. Quite

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some time ago, Sana et al.[15] used a method similar in the spirit of the G2 approach to give $\Delta_f H^\circ_{298}$ (HO_2) = 5.76 kcal mol^{-1}. Later, Francisco and Zhao[17] used quadratic configuration interactions using single, double, and perturbative triple excitations (QCISD(T)) to estimate $\Delta_f H^\circ_{298}$ (HO_2) = 5.1 ± 1.0 kcal mol^{-1}. Silica and Russo used density-functional theory[18] to determine the reaction enthalpy for $HO_2 + H \rightarrow H_2 + O_2$, giving an estimate of $\Delta_f H^\circ_{298}$ (HO_2) of 3.8 kcal mol^{-1}. Then, using several different reactions, Bauschlicher and Partridge obtained $\Delta_f H^\circ_{298}$ (HO_2) = 2.8 ± 0.5 kcal mol^{-1} (3.5 ± 0.5 kcal mol^{-1} at 0 K) from CCSD(T) single point energy calculations at reported experimental geometries.[19] Also, Walch and Duchovic[20] have reported a $\Delta_f H^\circ_0$ (HO_2) value of 4.1 kcal mol^{-1} using multireference configuration interaction methods. Hence, over the past decade or so, theoretical estimates have spanned a range of roughly 3 kcal mol^{-1} (3.5−6.5 kcal mol^{-1} at 0 K). Prior to 2002, there had been no reported estimate of $\Delta_f H^\circ$ (HO_2) using an ab initio model chemistry. An assessment of several such approaches for open-shell molecules was recently reported by Henry et al.[21] By use of several variations of G2, G3, complete basis set, and Wn methods,[42] the authors estimate $\Delta_f H^\circ_0$ (HO_2) to be between 3.6 and 4.0 kcal mol^{-1} using the atomization energy approach. In this work, we report results obtained with the most sophisticated theoretical approach yet applied to this problem, yielding not only a well-established value for $\Delta_f H^\circ_0$ (HO_2) but also a well-founded error estimate considerably smaller than those reported previously.

II. Theoretical Methods

Ab initio calculations in this work were performed using a local version of the ACESII program package.[22] The high-level coupled-cluster (beyond CCSDT) calculations were carried out with the string-based many-body code written by one of the authors.[23] Basis sets come from the Dunning hierarchy (aug-)cc-p(C)VXZ (X = D, T, Q, and 5).[24−26] All molecular structures were optimized at the all-electron CCSD(T) level using the cc-pVQZ basis set. Previous work[27] has demonstrated that structures obtained at this level of approximation are close to equilibrium geometries inferred from experiment. Effects of basis set augmentation and more appropriate treatment of core correlation effects are measured via single-point calculations using the aug-cc-pCVXZ (X = D, T, Q, and 5) series together with the extrapolation techniques described below.

Extrapolation procedures are used to achieve a best estimate of total electronic energies for the molecules under study. The self-consistent-field (SCF) and correlation energies are treated separately. First, the aug-cc-pCVXZ (X = 3 (T), 4 (Q), and 5) basis-set energies are used together with the exponential relation[28]

$$E_{SCF}(X) = E^{\infty}_{HF} + a \exp(-bX) \qquad (1)$$

where $E_{SCF}(X)$ is the SCF energy obtained with the aug-cc-pCVXZ bases, E^{∞}_{HF} the estimated Hartree−Fock limit, and a and b are additional fitting constants. The corresponding basis-set limit for the CCSD(T) correlation energy is estimated using the formula[29]

$$E_{CCSD(T)}(X) = E^{\infty}_{CCSD(T)} + \frac{c}{X^3} \qquad (2)$$

where $E_{CCSD(T)}(X)$ is the CCSD(T) correlation energy obtained with the aug-cc-pCVXZ basis set. The estimated basis-set limit CCSD(T) correlation energy and the additional constant c are determined from single-point-energy calculations with the aug-cc-pCVQZ and aug-cc-pCV5Z basis sets.

To this point, total electronic energies are given by

$$E_{electronic} = E^{\infty}_{HF} + E^{\infty}_{CCSD(T)} \qquad (3)$$

leaving neglect of correlation beyond CCSD(T) as the overwhelmingly most significant source of residual error. Procedures for estimating the magnitude of these residual correlation corrections (RCC) are less established[30] than those for E^{∞}_{HF} and correlation energies at a given level of approximation. We have used two schemes in this work to estimate the magnitude of this vitally important contribution, both of which involve a significant amount of computational labor. In the first (E_{RCC}), the difference between the basis-set limit CCSDT and CCSD(T) energies is estimated[31] and augmented with a contribution from connected quadruple excitations. The latter is estimated by the difference between CCSDTQ and CCSDT energies using the cc-pVDZ basis set and the frozen-core approximation. The second approach ($E_{RCC'}$) also includes a contribution for connected *pentuple* excitations and is calculated analogously, i.e., the difference between frozen-core CCSDTQP and CCSDT energies obtained with the cc-pVDZ basis. These corrections are then added to obtain final nonrelativistic electronic energies within the simple Born−Oppenheimer approximation, viz.

$$E_{electronic} = E^{\infty}_{HF} + E^{\infty}_{CCSD(T)} + E_{RCC} \qquad (4)$$

or the corresponding equation with the more sophisticated $E_{RCC'}$ correction. Beyond this, increments to the energy are applied for (1) the zero-point vibrational energy (E_{ZPE}), (2) scalar relativistic effects (E_{SR}),[32] (3) the diagonal Born−Oppenheimer energy (E_{DBOC}), and (for otherwise degenerate states of radicals) (4) spin−orbit coupling (E_{SO}). The first is obtained from CCSD(T)/cc-pVQZ anharmonic force fields calculated as in ref 33, and E_{SR} is evaluated by contracting the one-particle density matrix obtained at the CCSD(T)/aug-cc-pCVTZ level with the Darwin and mass-velocity operators. Because of program limitations, E_{DBOC} was calculated at the SCF level with the aug-cc-pVTZ basis and the formalism of Handy et al.[34] Experimental spin−orbit corrections were applied for the ^3P state of the oxygen atom and the $^2\Pi$ state of the hydroxyl radical.[35,36] Total energies for all species considered in this work (ground states of H, O, H_2, O_2, OH, and H_2O in addition to HO_2) are given in Table 1 along with magnitudes of the individual contributions described above.

III. Results and Discussion

A. Bond Energies. As an initial test of the accuracy of the computational method used to address the principal goal of this paper, an accurate estimate of the enthalpy of formation for the hydroperoxyl radical, we have used the same strategy to calculate BDEs in HOO and some related molecules since these quantities are known with reasonable precision. The bond energies of H_2,[37] O_2,[38] OH, and H_2O[39,40] have all been established to within 0.08 kcal mol^{-1}; the accuracy of our theoretical approach can therefore be tested to some degree by calculating these quantities. Results for these well-established bond energies are presented in Table 2. Given there are results obtained with and without the residual correlation corrections E_{RCC} and $E_{RCC'}$. Although an accuracy of ca. 1 kcal mol^{-1} is achieved for all three treatments of the correlation energy, the inclusion of quadruple and pentuple excitations reduces the error

TABLE 1: Energy Contributions (in kcal mol^{-1}) for Each of the Molecules Treated in This Study[a]

species	E_{HF}^{∞}	$E_{CCSD(T)}^{\infty}$	E_{RCC}	$E_{RCC'}$	E_{ZPC}	E_{SR}	E_{DBOC}	E_{SO}	total energy
H	−313.77					-4.086×10^{-3}	0.17		−313.60
O	−46949.82	−155.98	−0.26	−0.26		−32.92	1.484	−0.22	−47137.71
H_2	−711.38	−25.67			6.21	-5.97×10^{-3}	0.29		−730.57
O_2	−93933.18	−398.61	−1.09	−1.21	2.29	−65.64	2.96		−94393.40
OH	−47332.04	−194.72	−0.34	−0.35	5.31	−32.79	1.64	−0.20	−47553.15
H_2O	−47733.28	−233.18	−0.26	−0.27	13.33	−32.66	1.70		−47984.36
HO_2	−94285.33	−415.10	−0.98	−1.03	8.85	−65.56	3.14		−94755.03

[a] All contributions are described in section II; total energies are given in the rightmost column and correspond to those in which the highest level correlation correction is applied.

TABLE 2: BDEs (D_0) Calculated by the Procedures Described in the Text[a]

	without RCC	with E_{RCC}	with $E_{RCC'}$	exp
H−H	103.36	103.36	103.36	103.26 ± 0.001[b]
O−H	101.75	101.83	101.84	101.76 ± 0.07[c]
O−O	117.29	117.87	117.98	117.97 ± 0.03[d]
H−OH	117.69	117.61	117.61	117.59 ± 0.07[c]
H−OO	48.20	48.09	48.02	47.6 ± 0.8[e]
O−OH	63.74	64.12	64.16	64.3 ± 0.8[e]

[a] The leftmost column of numbers excludes contributions from higher than triple excitations, the third and fourth columns include quadruple and pentuple excitation corrections, respectively. All values are in kcal mol^{-1}. [b] From ref 37. [c] From ref 40. [d] From ref 38. [e] From ref 12.

by roughly an order of magnitude. By use of the $E_{RCC'}$ correction, these accurately known bond energies are all reproduced to within experimental error. The only exception is H_2, which is something of a special case,[41] where the calculated BDE is 0.1 kcal mol^{-1} above the exact value. It is notable, and important in the context of subsequent discussion, that the inclusion of pentuple excitations in the $E_{RCC'}$ correction is apparently necessary to bring the BDE of O_2 into agreement with experiment. Similar conclusions regarding the role of quadruple and higher excitations for the calculation of bond energies have been reached by Martin and co-workers in studies using the Wn methods.[42]

The agreement is also satisfactory for the two distinct bond energies in HO_2, although these are clearly less useful for calibrating the accuracy of the method due to relatively large experimental uncertainties. Pentuple excitations (as measured by the difference between bond energies based on E_{RCC} and $E_{RCC'}$) are evidently important here as well, at least on the 0.1-kcal mol^{-1} level of accuracy. However, these calculations are expected to be sufficiently accurate that we believe it justified to claim that the true H−O and O−O bond energies in peroxyl lay, respectively, above and below the center-of-gravity experimental estimates of Litorja and Ruscic.[12]

All things considered, we believe that assigning a computational uncertainty of 0.10 kcal mol^{-1} is quite reasonable, and perhaps even conservative, given the performance of the method for bond energies. This estimation will form the basis for estimates of uncertainty in the heats of formation discussed in the following subsection.

B. Enthalpies of Formation. Enthalpies of formation (at 0 K) were calculated in this work by a procedure analogous to the atomization energy approach widely used in the ab initio community for this purpose. In that approach, the energy of a molecule is evaluated by some particular computational procedure. This number is then subtracted from the energies of the constituent atoms as evaluated by the same computational approach, the difference being the atomization energy E_{AE}. Then the enthalpy of formation for molecule M can be trivially evaluated from

$$\Delta_f H^\circ\,(\mathrm{M}) = E_{AE} + \sum_J \Delta_f H^\circ\,(\mathrm{J}) \tag{5}$$

where the $\Delta_f H^\circ$ (J) are experimental atomic enthalpies of formation and the sum runs over all atoms in the molecule. This procedure has a number of advantages. First, once a database of atomic energies has been built, a determination of the enthalpy of formation for a particular molecule requires only calculations for that molecule. Moreover, there is usually little additional uncertainty that arises from application of eq 5 since atomic $\Delta_f H^\circ$ values are generally known to very high precision.[43]

One less satisfactory aspect of the atomization energy approach is that it is exceedingly difficult to calculate E_{AE} accurately by ab initio methods. It is far simpler to calculate energies of reactions in which the bonding environments of atoms on both sides of the chemical equation are not so dissimilar. In such cases, systematic errors in the calculation associated with particular chemical environments are allowed to cancel to some degree. This is the basic reason behind the success of so-called isodesmic reaction schemes (an isodesmic reaction is one in which the number and types of each chemical bond are preserved in the reaction).[44] In this work, we employ a scheme intermediate between the atomization energy and isodesmic approaches. Our strategy is to use a number of chemical reactions in which the enthalpy of formation of all species apart from the target species (ultimately hydroxyl radical) are known accurately from experiment.[45] The total energies for all species are calculated by the procedure outlined in section II; enthalpies of formation for the target species (M) are then calculated from

$$\Delta_f H^\circ\,(\mathrm{M}) = \frac{E_{rxn} - \sum'_J \nu_J \Delta_f H^\circ\,(\mathrm{J})}{\nu_M} \tag{6}$$

where E_{rxn} is the calculated reaction energy, the primed summation indicates that the species M is excluded, and ν_J is the stoichiometric coefficent of the species J in the chemical equation.

As an illustrative example of this approach, it is first applied to the hydroxyl radical (OH) for which $\Delta_f H_0^\circ$ is known to be 8.85 ± 0.07 kcal mol^{-1}.[39] Four reactions have been used, and the results are listed in Table 3. The first reaction ($H_2O + O \rightarrow 2OH$) is technically an isodesmic reaction; use of the third is of course equivalent to the atomization energy approach. The other two reactions have been chosen because of the accurately known enthalpies of formation for the reactants and other product species. The columns of Table 3 list the corresponding enthalpies of formation for OH that have been extracted from eq 6 using total energies that involve differing treatments of the vital residual correlation correction. It is apparent from the data in the table that inclusion of correlation effects beyond CCSD(T) significantly reduces the magnitude of scatter obtained from the different reactions. Without any treatment of RCC,

TABLE 3: Enthalpy of Formation Calculated for the Ground State of OH by Various Reaction Schemes[a]

reaction	$\Delta_f H_0^\circ$ (OH) without RCC	with E_{RCC}	with $E_{RCC'}$
$H_2O + O \rightarrow 2OH$	8.90	8.82	8.83
$H_2O + H \rightarrow OH + H_2$	8.85	8.77	8.78
$O + H \rightarrow OH$	8.86	8.78	8.78
$^1/_2H_2 + {}^1/_2O_2 \rightarrow OH$	8.58	8.78	8.84

[a] Details of the calculations are described in the text; the meaning of the three columns is the same as in Table 2. All values are in kcal mol^{-1}.

TABLE 4: Enthalpy of Formation Calculated for the Ground State of the Hydroperoxy Radical by Various Reaction Schemes[a]

reaction	$\Delta_f H_0^\circ$ (HO_2) without RCC	with E_{RCC}	with $E_{RCC'}$
$O_2 + H_2 \rightarrow HO_2 + H$	3.53	3.65	3.71
$O_2 + OH \rightarrow HO_2 + O$	3.42	3.62	3.69
$O_2 + {}^1/_2H_2 \rightarrow HO_2$	3.48	3.60	3.66
$O_2 + H \rightarrow HO_2$	3.43	3.55	3.61
$OH + O \rightarrow HO_2$	4.09	3.71	3.67
$H_2 + 2O \rightarrow HO_2 + H$	4.20	3.74	3.69
$H_2O + OH \rightarrow HO_2 + H_2$	4.08	3.71	3.67
atomization energy	4.10	3.64	3.59

[a] Details of the calculations are described in the text; the meaning of the three columns is the same as in Table 2. All values are in kcal mol^{-1}.

the results vary from 8.58 to 8.90 kcal mol^{-1}, the outlier being the reaction that involves the problematic molecular oxygen. However, with quadruple and pentuple excitations, differences between the highest and lowest values are reduced to 0.06 kcal mol^{-1}. All in all, these results confirm the estimate of Litorja and Ruscic[12] and show the accuracy that can be obtained by the present approach.

Let us now turn attention to the enthalpy of formation for the hydroperoxy radical (HO_2), which of course is the principal goal of this paper. Eight separate reactions have been chosen for this purpose, including one that corresponds precisely to the atomization energy approach. Results are listed in Table 4. Owing to the more challenging nature of the electronic structure of HO_2 (relative to OH) and the presence of molecular oxygen in a number of the reactions, the magnitude of the scatter is greater than that found in the OH calculations at each of the three levels. With calculations based on the CCSD(T) treatment of correlation (second column of Table 4), the inferred values of the enthalpy of formation range from 3.42 to 4.20 kcal mol^{-1}. However, the situation is dramatically improved when RCC corrections are added. By use of E_{RCC}, the scatter is reduced to 0.19 kcal mol^{-1} and the incorporation of pentuples in the $E_{RCC'}$ correction further reduces this to 0.12 kcal mol^{-1}. It is significant to note that the outlier in the highest-level calculations is that obtained from the atomization energy approach, which underscores the statement made above about the difficulty of calculating these quantities accurately. Another way of seeing this is that the treatment of RCC effects changes the value of $\Delta_f H_0^\circ$ obtained from the atomization energy scheme by 0.51 kcal mol^{-1}, while a similarly large effect is seen only for the equally misbalanced $H_2 + 2O \rightarrow HO_2 + H$ reaction (no bond types preserved). Taken as a whole, the present set of data makes a convincing case for $\Delta_f H_0^\circ$ (HO_2) to be near 3.65 kcal mol^{-1}, and we therefore recommend a value of $\Delta_f H_0^\circ$ (HO_2) of 3.66 ± 0.10 kcal mol^{-1}. We are confident that the exact value falls within the specified range of uncertainty.

Before concluding, some discussion of the excellent experimental work done on this problem is warranted. As can be seen in Figure 1, all previous estimates based on experimental studies are consistent with the value recommended here, in the sense that the value of 3.66 kcal mol^{-1} is within the uncertainty ranges of every study published in the past twenty years. Clearly, the major issue with respect to this problem has been the unacceptably large uncertainties associated with $\Delta_f H^\circ$ for HO_2 rather than any intrinsic lack of accuracy on the part of experimental work.

Finally, using heat-capacity corrections obtained from the NIST-JANAF tables,[7] a thermal correction ($\Delta_f H_{298}^\circ$ (HO_2) − $\Delta_f H_0^\circ$ (HO_2)) of −0.70 kcal mol^{-1} is obtained. Hence, the

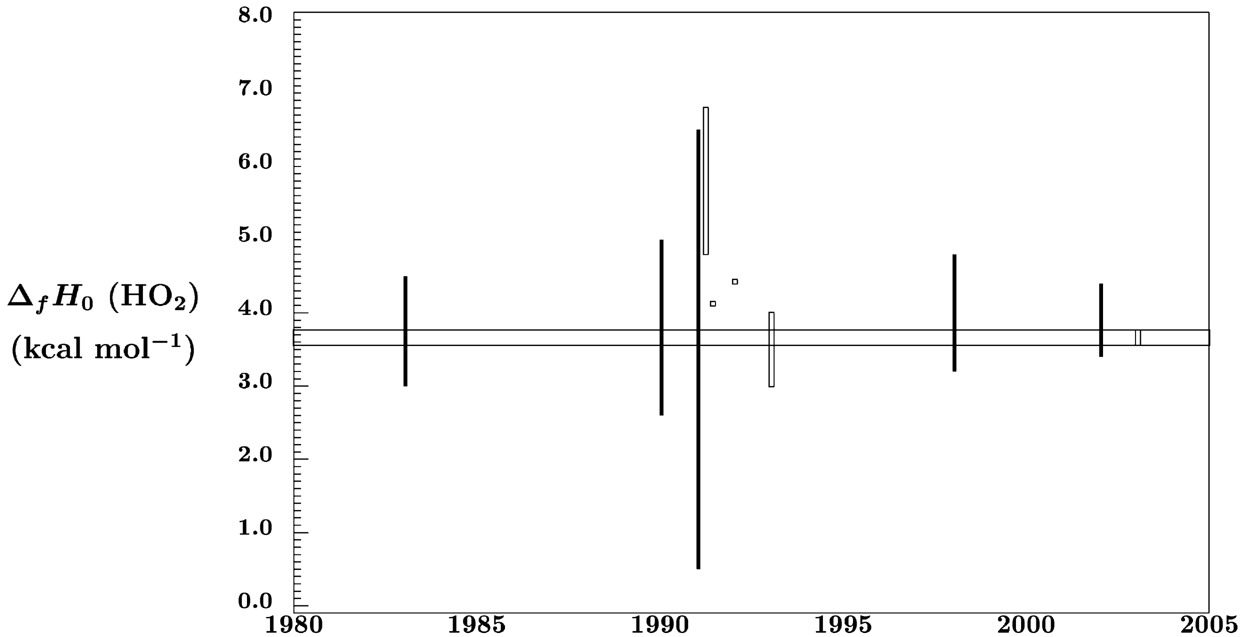

Figure 1. Ranges of estimated enthalpies of formation (at 0 K) for HO_2 radical in the past twenty years. Experimental estimates are shown by shaded rectangles, while theoretical results are unshaded. Theoretical values given without estimated uncertainties are designated by squares. The lines running across the figure show the range of values consistent with the present set of calculations.

recommended value of the perhaps more interesting $\Delta_f H^\circ_{298}$ (HO_2) value is 2.96 ± 0.10 kcal mol^{-1}.

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