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Active Thermochemical Tables: Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO_2[†]

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Through the use of the Active Thermochemical Tables approach, the best currently available enthalpy of formation of HO_2 has been obtained as $\Delta_f H_{298}°(HO_2) = 2.94 \pm 0.06$ kcal mol^{-1} (3.64 ± 0.06 kcal mol^{-1} at 0 K). The related enthalpy of formation of the positive ion, HO_2^+, within the stationary electron convention is $\Delta_f H_{298}°(HO_2^+) = 264.71 \pm 0.14$ kcal mol^{-1} (265.41 ± 0.14 kcal mol^{-1} at 0 K), while that for the negative ion, HO_2^- (within the same convention), is $\Delta_f H_{298}°(HO_2^-) = -21.86 \pm 0.11$ kcal mol^{-1} (-21.22 ± 0.11 kcal mol^{-1} at 0 K). The related proton affinity of molecular oxygen is $PA_{298}(O_2) = 100.98 \pm 0.14$ kcal mol^{-1} (99.81 ± 0.14 kcal mol^{-1} at 0 K), while the gas-phase acidity of H_2O_2 is $\Delta_{acid}G_{298}°(H_2O_2) = 369.08 \pm 0.11$ kcal mol^{-1}, with the corresponding enthalpy of deprotonation of H_2O_2 of $\Delta_{acid}H_{298}°(H_2O_2) = 376.27 \pm 0.11$ kcal mol^{-1} (375.02 ± 0.11 kcal mol^{-1} at 0 K). In addition, a further improved enthalpy of formation of OH is briefly outlined, $\Delta_f H_{298}°(OH) = 8.93 \pm 0.03$ kcal mol^{-1} (8.87 ± 0.03 kcal mol^{-1} at 0 K), together with new and more accurate enthalpies of formation of NO, $\Delta_f H_{298}°(NO) = 21.76 \pm 0.02$ kcal mol^{-1} (21.64 ± 0.02 kcal mol^{-1} at 0 K) and NO_2, $\Delta_f H_{298}°(NO_2) = 8.12 \pm 0.02$ kcal mol^{-1} (8.79 ± 0.02 kcal mol^{-1} at 0 K), as well as H_2O_2 in the gas phase, $\Delta_f H_{298}°(H_2O_2) = -32.45 \pm 0.04$ kcal mol^{-1} (-31.01 ± 0.04 kcal mol^{-1} at 0 K). The new thermochemistry of HO_2, together with other arguments given in the present work, suggests that the previous equilibrium constant for $NO + HO_2 \rightarrow OH + NO_2$ was underestimated by a factor of $\sim$2, implicating that the $OH + NO_2$ rate was overestimated by the same factor. This point is experimentally explored in the companion paper of Srinivasan et al. (next paper in this issue).

1. Introduction

The hydroperoxyl radical, HO_2, is a very important and reactive intermediate in combustion chemistry and in the atmosphere and is also present in interstellar clouds. The knowledge of its enthalpy of formation is crucial for accurate modeling of processes leading to its formation and destruction. The available experimental literature values for $\Delta_f H_{298}°(HO_2)$ span a very wide range between 0.5 ± 2 and 5 ± 2 kcal mol^{-1} (vide infra), even when the unusually low[1] and amply criticized[2−5] value of −6.9 kcal/mol is excluded. The aim of this paper is to firmly establish the best currently available enthalpy of formation of HO_2 using the new Active Thermochemical Tables (ATcT) approach.[6−8]

The highly accurate value for $\Delta_f H°(HO_2)$ presented here has, inter alia, significant ramifications for the equilibrium constant of the $NO + HO_2 \rightarrow OH + NO_2$ reaction, which is of major importance in stratospheric ozone depletion. The veracity of the resulting implications is further tested and validated in the companion paper[9] (the following paper in this issue), which reports on a new high temperature determination of the $OH + NO_2$ kinetic rate.

1.1. Active Thermochemical Tables. The recently developed Active Thermochemical Tables are a new paradigm of how to obtain reliable, accurate, and internally consistent thermochemistry.[6−8] Traditional sequentially developed thermochemical compilations implicitly contain a hidden maze of progenitor−progeny dependencies between the enthalpies of formation of different chemical species and use the available thermochemical information only partially.[6] As opposed to sequential thermochemistry, ATcT utilizes the Thermochemical Network (TN) approach. TN does not store enthalpies of formation of various chemical species as such; rather, it stores the relevant underlying determinations, such as reaction enthalpies, bond dissociation energies, and equilibrium constants, and hence it explicitly uses (and keeps track of) the interdependencies between thermochemical properties of the involved species. As the underlying knowledge contained in the TN is expanded by inserting additional thermochemically relevant determinations, an updated and consistent set of enthalpies of formation can be promptly found by simultaneously solving the whole TN. Finding the TN solution involves a detailed iterative statistical analysis, which has the role of identifying the interdependencies (measurements and/or high-quality computations) that may have

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TABLE 1: Available Experimental Values for the Standard Enthalpy of Formation of HO_2 at 298 K (in kcal mol^{-1})[a]

source	originally reported value[b]	revised value[c]
JANAF Tables[10,11]	0.5 ± 2.0	
Gurvich et al.[19]	2.3 ± 0.7	
Howard[20]	2.5 ± 0.6	2.0 ± 0.6
Lee and Howard[21]	3.3 ± 0.6	3.2 ± 0.6
Hills and Howard[23]	3.0 ± 0.4	2.9 ± 0.4
Shum and Benson[24,25]	>3.0	
Heneghan and Benson[26]	4.6 ± 0.2	
Heneghan and Benson[29]	>3.4	
Fisher and Armentrout[30]	3.8 ± 1.2	3.2 ± 1.2
Litorja and Ruscic[31]	3.3 ± 0.8	2.9 ± 0.6[d]
Clifford et al.[32]	3 ± 1	
Ramond et al.[35]	3.2 ± 0.5	3.2 ± 0.5
ATcT, current work[e]	2.94 ± 0.06	

[a] Except for the ATcT value in the last row, all enthalpies of formation in this table were obtained by a traditional sequential approach to thermochemistry. [b] As originally reported by the source authors.[c] The value from the same experimental data when the best currently available auxiliary thermochemical values[6,19,59−62] are utilized for interpretation. Most (but not all, see text for more information) of the revisions are related to the new enthalpy of formation of OH.[58−60] [d] Involves refitting of the original photoionization experiment; see text for details. [e] The ATcT value has been obtained not by sequential thermochemistry but by simultaneous solution of C(A)TN; see text.

"optimistic" uncertainties and hence tend to skew the resulting enthalpies of formation. The discovery of unrealistic uncertainties is made possible by the inherent redundancies present in the interdependency manifold of the TN.

Compared to the traditional sequential approach to thermochemistry, ATcT offers a number of significant advantages and several totally new features.[6−8] Of primary relevance in the present context is that the enthalpies of formation (and the associated uncertainties) obtained from ATcT are inherently superior to those obtained traditionally, because they properly reflect *all* the knowledge that is stored in the TN. For a more detailed description of the ATcT approach, and its other novel aspects, such as rapid update with new knowledge and its painless propagation through all the affected values, hypothesis testing ability, generation of pointers to new experiments, availability of the complete covariance matrix, and so forth, together with a few practical examples that illustrate the ATcT capabilities, we refer the reader to the introductory paper by Ruscic et al.[6]

1.2. Overview of Existing Values of the Enthalpy of Formation of HO_2. The popular 3rd edition of JANAF Tables[10] recommends $\Delta_f H_{298}°(HO_2) = 0.5 \pm 2.0$ kcal mol^{-1} (see middle column of Table 1), which persists even in the latest (4th) edition[11] and is the value currently listed in the NIST WebBook.[12] The value is based on measurements involving[13] $O_2 + HX \rightarrow HO_2 + X$ (X = Cl, Br, I), and the proton affinity[14,15] of O_2, and is a sharp downward revision of the previous JANAF recommendation (5 ± 2 kcal mol^{-1} in the 2nd edition[16] from electron impact measurements of Foner and Hudson[17]).

The Gurvich Tables (3rd Russian edition[18]) similarly recommended 0.5 ± 1.0 kcal mol^{-1}, but this was revised for the English translation[19] to $\Delta_f H_{298}°(HO_2) = 2.3 \pm 0.7$ kcal mol^{-1}. The revision was based primarily on Howard,[20] who derived $\Delta_f H_{298}°(HO_2) = 2.5 \pm 0.6$ kcal mol^{-1} by third-law analysis of the equilibrium constant for $NO + HO_2 \rightarrow OH + NO_2$, obtained from kinetics studies of forward and reverse rates. However, as noted by Howard, the second-law analysis of the same equilibrium constant produces $\Delta_f H°(HO_2)$ values that are up to 1 kcal mol^{-1} higher. We will return to this point later. Lee and Howard[21] subsequently suggested $\Delta_f H_{298}°(HO_2) = 3.3 \pm 0.6$ kcal mol^{-1} from their measurements of the rate constant and branching ratio for $Cl + HO_2$ (producing $HCl + O_2$ and $OH + ClO$), which were coupled to a literature value[22] for the reverse rate ($OH + ClO$). Partly in response to critiques by Benson, who advocated higher values (vide infra), Hills and Howard[23] later undertook their own determination of the reverse rate (and the related branching ratios) needed to complete the equilibrium constant for $Cl + HO_2 \rightarrow OH + ClO$, thus obtaining $\Delta_f H_{298}°(HO_2) = 3.0 \pm 0.4$ kcal mol^{-1}.

Criticizing the value of Howard[20] as too low, Shum and Benson[24,25] at first advocated a lower limit $\Delta_f H_{298}°(HO_2) > 3.0$ kcal mol^{-1}, based on estimated A factors and an upper limit to the rate for $HI + O_2 \rightarrow HO_2 + I$ and the analogous $HCl + O_2$ and $HBr + O_2$ reactions. Shortly thereafter, Heneghan and Benson[26] proposed $\Delta_f H_{298}°(HO_2) = 4.6 \pm 0.2$ kcal mol^{-1}, derived from their D_{298}(*t*-BuOO−H) (subsequently shown to be too high[27]) using the questionable assumption[28] (particularly in view of the quoted uncertainty of ±0.2 kcal mol^{-1}) that the O−H bond dissociation enthalpies in *t*-BuOOH and H_2O_2 are the same. In a parallel study of the rate for $Br + H_2O_2 \rightarrow HO_2 + HBr$, combined with an estimation of A factors to infer the activation energy, Heneghan and Benson[29] estimated $\Delta_f H_{298}°(HO_2) > 3.4$ kcal mol^{-1}, suggesting a value as high as 4.1 kcal mol^{-1}.

The controversy of the low vs high value of $\Delta_f H°(HO_2)$ received new life when Fisher and Armentrout[30] determined $\Delta_r H°(O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2) = 4.6 \pm 1.2$ kcal mol^{-1} using guided ion beam techniques and, with auxiliary thermochemical data available at the time, derived $\Delta_f H_{298}°(HO_2) = 3.8 \pm 1.2$ kcal mol^{-1}.

More recently, Litorja and Ruscic[31] performed a photoionization study of the HO_2 radical and the H_2O_2 parent molecule and determined the adiabatic ionization energy of HO_2, EI(HO_2) = 11.352 ± 0.007 eV, and the 0 K appearance energy of the HO_2^+ fragment from H_2O_2, AE(HO_2^+/H_2O_2) = 15.112 ± 0.035 eV. The resulting positive ion cycle produced $\Delta_f H_{298}°(HO_2) = 3.3 \pm 0.8$ kcal mol^{-1}.

At about the same time, Clifford et al.[32] measured the electron affinity EA(HO_2) = 1.089 ± 0.006 eV (see also ref 33). Rather than use the enthalpy of deprotonation (related to gas-phase acidity) available at the time,[34] $\Delta_{acid}H_{298}°(H_2O_2) = 375.5 \pm 3.3$ kcal mol^{-1}, to close the negative ion cycle, which would have produced $\Delta_f H_{298}°(HO_2) = 2.4 \pm 3.3$ kcal mol^{-1}, Clifford et al.[32] judiciously took the opposite route and derived an improved $\Delta_{acid}H_{298}°(H_2O_2) = 376 \pm 1$ kcal mol^{-1} by adopting $\Delta_f H_{298}°(HO_2) = 3 \pm 1$ kcal mol^{-1} (average of Howard's values[20,21,23]). The same group (Ramond et al.[35]) has subsequently remeasured both $\Delta_{acid}H_{298}°(H_2O_2) = 376.5 \pm 0.4$ kcal mol^{-1} and EA(HO_2) = 1.078 ± 0.006 eV, from which $\Delta_f H_{298}°(HO_2) = 3.2 \pm 0.5$ kcal mol^{-1}, in outstanding agreement with the positive ion cycle result of 3.3 ± 0.8 kcal mol^{-1} by Litorja and Ruscic.[31]

Earlier theoretical values[36−43] for $\Delta_f H_{298}°(HO_2)$ have been summarized previously by Litorja and Ruscic.[31] Most of these tended to be quite high (4−6 kcal mol^{-1}), with the exception of the CCSD(T) value of 2.8 ± 0.5 kcal mol^{-1} by Bauschlicher and Partridge[42] and the QCISD(T) (including various corrections) value of 2.9 ± 0.2 kcal mol^{-1} by Karkach and Osherov.[43] Recent theoretical results cluster around ~3 kcal mol^{-1}, such as the G3(MP2)B3 value of 3.2 kcal mol^{-1} by Janoschek and Rossi[44] and the W1 result of 3.0 (± 0.7) kcal mol^{-1} by Parthiban and Martin.[45] The most recent theoretical result of 2.96 ± 0.10 kcal mol^{-1} was reported by Flowers et al.[46] from CCSD(T)/

aug-cc-pCV5Z calculations extrapolated to the basis-set limit, with additional scalar relativistic, spin−orbit coupling, and diagonal Born−Oppenheimer corrections, inclusion of anharmonic vibrational zero-point energies, as well as various empirical corrections that account for correlation effects not treated at the CCSD(T) level.

2. ATcT Approach

The new thermochemical values presented in this work are obtained by using the Active Thermochemical Tables approach.[6] The ingredients are the ATcT Kernel program and the underlying libraries that contain thermochemically relevant data.

2.1. ATcT Kernel. The Active Thermochemical Tables Kernel (currently at version 1.25) is the software embodiment of the ATcT approach.[6−8] The pertinent details of the strategy behind the ATcT approach and the essential mathematical equations have been presented previously.[6] The central role of the ATcT Kernel is to construct the manifold of interdependencies that define the Thermochemical Network (TN) using the underlying thermochemically relevant determinations, statistically analyze the TN, and, after iteratively adjusting any "optimistic" uncertainties, find the simultaneous solution for all chemical species present in the TN.[6−8] The iterative adjustment follows the currently implemented "worst offender" strategy, which uses feedback from a sequence of trial solutions until self-consistency across the whole TN is achieved.[6] The thermochemical values presented here were obtained by using the finest currently implemented adjustment step, which limits the augmentation of the "offending" uncertainty to 2% per iteration. Each adjustment slightly reduces the proportional weight of the corresponding determination in the TN, allowing the next iteration to move closer to the consensus solution set. The other relevant functions of the ATcT Kernel are related to retrieving the thermochemistry for the desired species from the simultaneous solution and computing on demand the full temperature-dependent complement of thermochemical functions using the available partition-function related data (such as spectroscopic constants, measured heat capacities, etc.)

2.2. Core (Argonne) Thermochemical Network. The Core (Argonne) Thermochemical Network,[6,8] C(A)TN, is the primary source of thermochemical data that exposes the interdependency manifold to the ATcT Kernel. The current version (1.052) of C(A)TN, which was utilized in the present work, contains >6400 thermochemically relevant determinations interlinking >700 thermochemically distinct species. C(A)TN contains a mixture of available experimental and theoretical data from the literature, as well as measurements and computations from our laboratory.

As opposed to fragmented *localized* TNs (which can also be treated and solved using the ATcT Kernel), C(A)TN corresponds to an ab ovo TN.[6] A localized TN is based on the assumption that a set of auxiliary enthalpies can be fixed at chosen values based on prior knowledge. If such artificial constraints are judiciously chosen, then a localized TN can occasionally be useful for exploratory constructs.[6,47,48] In an ab ovo TN, no such constraints exist and the only enthalpies of formation/Gibbs energies of formation that are fixed are the reference states of the elements. Localization constraints are sometimes temporarily imposed to C(A)TN to perform various exploratory analyses when a new species is inserted (such as evaluating the integrity of partition-function related information). All results presented here were obtained from the unconstrained C(A)TN.

Before insertion into the TN, all data and the associated uncertainties are critically evaluated and, in a fair number of cases, reinterpreted. A valiant attempt is made to also evaluate realistic 95% confidence limits of the original measurement, which is the expected (and assumed) coverage level of uncertainties in thermochemistry.[49,50] It should be noted here that all initially assigned uncertainties are subsequently reevaluated during the statistical analysis of the TN, which is an integral part of the normal ATcT approach.

All critically evaluated experimental data is inserted in a form that is as close as practical to the original measurement (e.g., third-law Gibbs energy and second-law enthalpy of a reaction at the temperature corresponding to the midpoint of the measured range, individually determined components for ion cycles, Gibbs energies for ion−molecule reactions determining relative proton affinities and gas-phase acidities, etc.) and in the original units of measurement.

In cases of theoretical results, eligible quantities are the atomization enthalpy (generally at 0 K), the computed bond dissociation energy, or the computed enthalpy of the isodesmic/isogyric reaction as actually used by the authors. For ions, eligible computational quantities include adiabatic ionization energies and electron affinities or computed enthalpies of ion−molecule reactions. With rare exceptions, the computed enthalpies of formation are derived quantities that are not independent of other (experimental) data and are ineligible for insertion into C(A)TN.

Theoretical literature has, unfortunately, a serious propensity toward under-representing the uncertainties.[50] In most cases, before the results could be entered in the C(A)TN, the reported (or implied) uncertainties needed to be rescaled by experience-based factors to bring them closer to the desired 95% confidence interval, using, where available, the reported MAD (mean absolute deviation) for the method scaled by a factor of 2 as a rough guide.

Theoretical determinations from the literature were complemented by additional computations in our laboratory, using popular composite electronic structure methods, such as G3//B3LYP,[51] G3,[52] and also CBS-Q, CBS-QB3, and CBS-APNO.[53−56] All new calculations were performed using the Gaussian 03 suite of programs.[57] For methods that are not explicitly parametrized to include corrections for spin−orbit effects in the atomization asymptote, the atomization energies were used only when such effects were small compared to the expected uncertainty of the method.

Given the inherent complexities of a TN encompassing several thousand determinations, discussing the full details of C(A)TN is significantly beyond the scope and space constraints of any single paper. Rather, the pertinent details are being exposed through a series of related papers that report on new thermochemistry for various target chemical species and discuss the subset of relevant measurements present in the C(A)TN. This approach was ushered by the paper that introduced ATcT,[6] where new thermochemical values for a handful of "key" chemical species were reported and the relevant portions of the network dependencies were exposed and discussed. While the present paper mentions several related ATcT enthalpies of formation, the intended focus is on the HO_2 species.

3. Results and Discussion

3.1. Initial Analysis of the Equilibrium Constant for NO + HO_2 → OH + NO_2. Here, we would like to briefly follow up on the fact that Howard's[20] equilibrium constant for NO + HO_2 → OH + NO_2 tends to produce from second-law analysis (i.e., from the slope in a van't Hoff plot) an enthalpy of this reaction that is 0.6−1.1 kcal mol^{-1} *lower* (more negative, implying enthalpies of formation of HO_2 that are *higher*) than

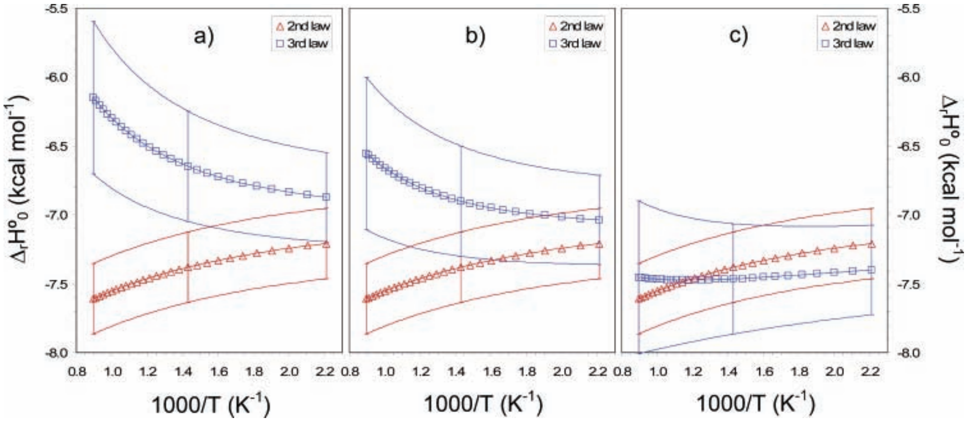

Figure 1. Thermochemical analysis of internal consistency of $K_{eq}(NO + HO_2 \rightarrow OH + NO_2)$ obtained from the forward and reverse rate constants measured by Howard.[20] The plots display the enthalpy of reaction at 0 K, $\Delta_rH_0°(NO + HO_2 \rightarrow OH + NO_2)$, as derived from second-law $\Delta_rH_T°$ (triangles) and third-law $\Delta_rG_T°$ (squares) at various T along the common range of validity. Though all derived $\Delta_rH_0°$ values should ideally be exactly the same, some level of discordance between second-law and third-law values from kinetic and equilibrium data is not uncommon and is acceptable if properly contained within the uncertainties. (a) $K_{eq}(NO + HO_2 \rightarrow OH + NO_2)$ is taken at face value. The third-law and second-law values show only an overlap of the tips of the error bars at the low-temperature end. The central values have no overlap. Overall, the level of discordance between the third-law and second-law values exceeds the individual uncertainties, indicating a problem with the K_{eq}. (b) K_{eq} has been artificially uniformly increased by 20%, thus preserving the second-law slope but shifting down the absolute third-law values. The overlap between the third-law values and second-law values at the low-temperature end becomes more convincing. The central values begin to show overlap of the tips of the uncertainties. (c) K_{eq} has been multiplied by a factor of 1.8. With factors close to 2, the internal inconsistencies of the measured K_{eq} are largely removed, and the third-law values fall within the uncertainties of the second-law values and vice versa along the whole temperature range.

the third-law analysis (i.e., from the absolute values of the equilibrium constant). In general, some level of discordance between second-law and third-law values from kinetic and equilibrium data is not uncommon. However, when the discrepancy is larger than the associated uncertainties, this becomes an indication of some underlying problem. The two most straightforward (and most common) sources of problems are an insufficient temperature range (producing an incorrect slope and thus frustrating the second-law analysis) or errors in determining the absolute value of the equilibrium constant (thus vitiating the validity of the third-law value). In the current case, the first of the two is not very likely to explain the problem, since the common temperature range between the forward and reverse kinetics rates of Howard is reasonably large (452−1115 K).

It should be duly noted here that the actual derivation of $\Delta_rH_T°$ by second-law and $\Delta_rG_T°$ by third-law at various temperatures along the common validity range does not require any auxiliary thermochemical data. It is the conversion from $\Delta_rG_T°$ to $\Delta_rH_T°$ and from $\Delta_rH_T°$ at various temperatures to $\Delta_rH_{T\text{common}}°$ (e.g., 0 or 298 K, used for intercomparing the reaction enthalpies) that demands the use of some auxiliary thermochemical data, but the needed knowledge is limited to the partition-function related properties (enthalpy increments—also known as integrated heat capacities—and entropies) of the involved species at the involved temperatures, which are, for the gas phase, based on spectroscopic constants of the individual species. Actual auxiliary values of enthalpies of formation become necessary only when the derived $\Delta_rG°$ and/or $\Delta_rH°$ for the reaction are utilized in the traditional sequential thermochemistry approach to derive the enthalpy of one of the species involved, by assuming that the others are known.

Since the forward and reverse rates of Howard are simple Arrhenius expressions, the slope in a van't Hoff plot is constant (−7.1 ± 0.3 kcal mol^{-1} at all temperatures). This is best interpreted as the enthalpy of reaction at the central temperature of the validity range. If this is nevertheless interpreted as being the reaction enthalpy along any and all points within the temperature range of validity, then the resulting $\Delta_rH_0°$ span the range between −7.2 and −7.6 kcal mol^{-1}. Though one would desire to see a constant value for $\Delta_rH_0°$, the amount of "sliding" along the temperature range is acceptable, since it is still correctly described (i.e., properly contained within the error bars) by $\Delta_rH_0° = -7.4 \pm 0.3$ kcal mol^{-1} which can be obtained from the central $\Delta_rH_T°$ value.

The third-law values for $\Delta_rH_0°$, converted from $\Delta_rG_T°$, span the range between −6.8 ± 0.4 kcal mol^{-1} at the low-temperature end and −6.2 ± 0.6 kcal mol^{-1} at the high-temperature end. The central value corresponds to −6.6 ± 0.4 kcal mol^{-1}. Again, the amount of sliding along the temperature range is acceptable, since it is correctly contained by the uncertainty of the central value. However, the third-law indeed produces a $\Delta_rH_0°$ that is less negative than the second-law value by 0.4 kcal mol^{-1} at the low T end and 1.4 kcal mol^{-1} lower at the high T end (see Figure 1a). What is really relevant, though, is that, within the stated uncertainties, the second-law and third-law values have only a small overlap of the very tips of the error bars at the low T end and no overlap throughout the rest of the range. In particular, the two central values have no overlap.

If one now were to assume that the absolute value of the equilibrium constant should be, for example, 20% larger (not an implausible assumption for most kinetic experiments), then this slightly shifts the third-law values and the overlap with the second-law value slightly improves at the low T end (see Figure 1b). A 20% increase is insufficient enough to remove the internal inconsistency between the second-law and third-law values, but it hints toward a possible solution. To get a convincing overlap, such that third-law values fall within the uncertainties of the second-law values and *vice versa* along the whole temperature range (see Figure 1 c), one would need to multiply the equilibrium constant by a factor of almost 2 (in fact, ∼1.8). Upon introduction of such a factor, the second-law and the third-law values begin to agree, resulting in $\Delta_rH_0° \sim -7.4 \pm 0.3$ and −7.5 ± 0.4 kcal mol^{-1}, respectively, which is about 0.8 kcal mol^{-1} more negative than the value selected by Howard,[20] and if accepted, it would increase by the same amount the $\Delta_fH°(HO_2)$ that would be obtained from his data.

It is also interesting to note that, if Howard have had relied on the second-law value, instead of favoring the third-law value, his proposed $\Delta_fH°(HO_2)$ would have been higher by the same amount.

3.2. Changes in Existing Values for $\Delta_f H°(HO_2)$. As seen in the "originally reported value" column of Table 1, the almost identical values for $\Delta_f H°(HO_2)$ obtained by traditional sequential thermochemistry from the positive and negative ion cycles tend to corroborate several previous results that cluster around 3 kcal mol^{-1}. However, some of the results in the middle column of Table 1 are pegged to the value of $\Delta_f H°(OH)$, which has been recently revised downward[58,59] by ~0.5 kcal mol^{-1} and hence need to be revised accordingly. This, though, does not necessarily mean that the affected $\Delta_f H°(HO_2)$ should simply be lowered by the same amount. Namely, while one result relied on $\Delta_f H°(OH)$ from the Gurvich Tables,[18,19] others relied on the even older value from JANAF,[10,11] which appears to suffer from a transcription error.[59] In addition, the enthalpy increments for OH given in JANAF[10,11] are also incorrect, causing erroneous temperature conversions for the related reaction enthalpies.[59]

3.2.1. Consequences of the Revised $\Delta_f H°(OH)$ on Kinetic Values for $\Delta_f H°(HO_2)$. Because of the mentioned peculiarities of the JANAF data for OH, using the currently recommended[59,60] $\Delta_f H°(OH)$, together with correct[19,60] enthalpy increments, has only a marginal (0.1 kcal mol^{-1}) effect on the kinetics values from Lee and Howard[21] and Hills and Howard[23] (see the right-hand column of Table 1). However, the reported third-law value of Howard[20] shifts downward by the full 0.5 kcal mol^{-1} amount, to $\Delta_f H_{298}°(HO_2) = 2.0 \pm 0.6$ kcal mol^{-1}, moving it away from the "consensus". (The second-law value, had it been selected by Howard, would have now become ~2.8 kcal mol^{-1}, quite close to the consensus.)

Though unrelated to the OH enthalpy, the "high" value of Fisher and Armentrout[30] (3.8 ± 1.2 kcal mol^{-1}) becomes 3.2 ± 1.2 kcal mol^{-1}, once their measured enthalpy of the ion–molecule reaction $\Delta_r H°(O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2) = 4.6 \pm 1.2$ kcal mol^{-1} is coupled to the best currently available auxiliary thermochemical values[6,61,62] for CH_4, CH_3^+, and O_2^+.

3.2.2. Revision of the Photoionization Threshold for AE(HO_2^+/H_2O_2). Besides the kinetic data from Howard's group, the revised enthalpy of formation of OH also affects one of the measurements involved in the positive ion cycle of Litorja and Ruscic.[31] However, here, the dependence on OH is indirect and requires refitting the photoionization onset of HO_2^+ from H_2O_2.

Litorja and Ruscic[31] originally reported AE(HO_2^+/H_2O_2) = 15.112 ± 0.035 eV as the 0 K value for this threshold. As they discussed, the $HO_2^+ + H + e^-$ is not the lowest-energy threshold in the dissociative photoionization of H_2O_2 and has a complex shape that cannot be simply described by the usual single-kernel approach,[63−70] but it can be described with two kernels, one describing the immediate threshold region (the *lower* kernel) and the second describing the behavior of the fragment ion yield curve at slightly higher energy (the *upper* kernel). (In the context of photoionization spectroscopy, the "kernel" is the appropriate basic functional form that adequately describes the photoionization cross-section for a fragmentation process in the absence of thermal effects. The single-kernel approach is adequate when the fragmentation can be described in the desired threshold region by a single process. If there is more than one process, that is, if there are additional processes sequentially opening up at higher energies, then a multiple-kernel approach is needed.) The drawback of the double-kernel requirement is that it doubles the number of free parameters available to the fit and makes the extracted thermochemical onset, which is one of the fitted parameters, less convincing. The threshold for $H_2O_2 \rightarrow HO_2^+ + H + e^-$ is preceded immediately by the threshold for $H_2O_2 \rightarrow OH^+ + OH + e^-$, which can be measured separately because it appears at a different mass in the mass spectrometer. Fortuitously, the two fragment ion yield curves have a very similar shape. In particular, the *upper* portions of the two curves can be almost completely superimposed by simply shifting them on the energy scale. Hence, Litorja and Ruscic[31] devised an approach in which the OH^+ threshold is fitted first, but the (presumably known) thermochemical onset described by the *lower* kernel for this process is kept fixed, thus reducing the number of free parameters. The fit delivers the essential parameters of the *upper* kernel, some of which are then reutilized as fixed parameters for a double-kernel fit of the HO_2^+ threshold. In this second fit, the *lower* kernel produces the targeted AE(HO_2^+/H_2O_2) thermochemical threshold as one of the fitted parameters.

Clearly, if during the first double-kernel fit the assumed thermochemical threshold for $H_2O_2 \rightarrow OH^+ + OH + e^-$, which fixes the far end of the *lower* kernel, is incorrect, then this will tend to affect the fitted parameters of the *upper* kernel, which may in turn influence the fitted threshold of the *lower* kernel of the second fit. The revision of the enthalpy of OH downward by ~0.5 kcal mol^{-1} shifts the assumed energy of the $H_2O_2 \rightarrow OH^+ + OH + e^-$ threshold by ~1.0 kcal mol^{-1}, which is a rather significant amount. Therefore, one expects that the real thermochemical onset for HO_2^+ is also likely to be lower than the originally reported value, though the shift should be much less than 1.0 kcal mol^{-1}, given the fact that the relationship between the two thresholds is indirect.

When the original data of Litorja and Ruscic is refitted with revised values for OH and OH^+ while using the original procedure, the resulting fit produces a threshold for the appearance of the HO_2^+ fragment from H_2O_2 that is slightly lower: EA(HO_2^+/H_2O_2) = 15.095 ± 0.026 eV. Though the new fits appear visually very similar to the original ones, the change in the reference threshold must be producing an inherently better fit of these difficult thresholds, since the resulting uncertainty in the target threshold is now somewhat lowered. The shift of the target threshold (0.017 eV = 0.4 kcal mol^{-1}) is modest compared to that of the indirect reference (1 kcal mol^{-1}) and is, in fact, still contained within the uncertainty of the initial value given by Litorja and Ruscic. The use of EI(HO_2) = 11.352 ± 0.007 eV of Litorja and Ruscic,[31] with the refitted EA(HO_2^+/H_2O_2), produces $D_0(H-O_2H) = 86.3 \pm 0.6$ kcal mol^{-1}, corresponding to $\Delta_f H_{298}°(HO_2) = 2.9 \pm 0.6$ kcal mol^{-1}.

As seen by inspecting the right-hand column of Table 1, the revised values for $\Delta_f H_{298}°(OH)$ are quite tightly clustered around ~3 kcal/mol and are in excellent agreement within their respective uncertainties, with one tell-tale exception: the third-law value obtained from the equilibrium constant for $NO + HO_2 \rightarrow OH + NO_2$ of Howard[20] is lower than the rest. The clearly noticeable gap between this value and the emerging consensus is the first indicator suggesting a problem with the underlying equilibrium constant.

3.2.3. Summary of the Revised Values for $\Delta_f H_{298}°(HO_2)$ Using Sequential Thermochemistry. Though within the traditional sequential thermochemistry approach the selection of the recommended value for $\Delta_f H_{298}°(HO_2)$ depends on the attitude of the evaluator and is hence highly subjective, the prevailing approach would be to simply embrace and recommend the single best currently available value experimental value for $\Delta_f H_{298}°(HO_2)$, which is that of Hills and Howard, 2.9 ± 0.4 kcal mol^{-1}. Alternatively, a more cautious evaluator might decide to recommend a properly weighted average of the revised values in the right-hand column of Table 1 (excluding the dissonant value of Howard[20]), thus producing a consensus value of $\Delta_f H_{298}°(HO_2) = 3.0 \pm 0.5$ kcal mol^{-1}. In either case, the final value that might be recommended via the traditional sequential approach would be based on partial use of the available information. As we shall show below, ATcT is able to use more completely and efficiently the available thermochemical information, producing a value that is significantly more accurate.

3.3. New Thermochemical Values from ATcT using C(A)TN. 3.3.1. Relevant HO_2 Thermochemical Dependencies in C(A)TN. As mentioned before, C(A)TN is not built upon various derived enthalpies of formation, such as those given in Table 1. Instead, C(A)TN contains the relevant determinations, such as reaction enthalpies and Gibbs energies that result from the original measurements without recourse to any auxiliary enthalpies of formation. Within the current version of C(A)TN, the HO_2 species and its positive and negative ions, HO_2^+ and HO_2^-, are robustly connected by more than 70 experimental and theoretical determinations to 28 "first neighbor" species (such as H_2O_2, H_2O, OH, O_2, O_2^+, H, H^+, O, O^-, C_2H_2, C_2H^-, CH_4, CH_3^+, NO, NO_2, ClO, Cl, CF_3H, CF_3^-, HF, F^-, HNO_3, etc.), which are then cross-connected to the remainder of the TN through other relevant dependencies.

A substantial number of relevant determinations have been mentioned above. Thus, for example, C(A)TN contains the third-law determination of the Gibbs energy for $Cl + HO_2 \rightarrow OH + ClO$ of 0.00 ± 0.34 kcal mol^{-1} at 298 K by Lee and Howard[21] (which includes the data of Leu and Lin[22]), together with the third-law Gibbs energy of 0.31 ± 0.24 kcal mol^{-1} at 293 K by Hills and Howard.[23] It also contains the Gibbs energy at 298 K of 0.57 ± 0.34 kcal mol^{-1} estimated for the same reaction by Kegley-Owen et al.[71]

The determinations resulting from Howard's measurements[20] of the forward and reverse rates of $NO + HO_2 \rightarrow OH + NO_2$ are entered as the second-law enthalpy of the reaction of −7.2 ± 0.3 kcal mol^{-1} and the third-law Gibbs energy of reaction of −4.3 ± 0.4 kcal mol^{-1}, both at 676 K. Though, as discussed (vide supra), there are strong a priori indications that these are probably not entirely congruent, no further biases or constraints on these measurements were introduced at the stage of constructing the C(A)TN dependencies for HO_2, allowing the ATcT iterative analysis of the TN to make the final determination.

C(A)TN also includes the experimental determinations of the adiabatic ionization energy of HO_2 of 11.35 ± 0.01 eV of Dyke et al.[72] and 11.352 ± 0.007 eV of Litorja and Ruscic,[31] together with the corresponding theoretical values from targeted electronic structure computations: 11.350 ± 0.095 eV (G3//B3LYP), 11.354 ± 0.099 eV (G3), 11.357 ± 0.175 eV (CBS-Q), 11.395 ± 0.099 eV (CBS-QB3), and 11.314 ± 0.075 eV (CBS-APNO), where the assigned uncertainties are rough empirical estimates of the 95% confidence limits of the respective methods. Similarly, the TN contains the experimental adiabatic electron affinity of 1.078 ± 0.006 eV obtained by Ramond et al.[35] and also reinterpreted from the data of Clifford et al.[32,35,73] and 1.078 ± 0.017 eV from Oakes et al.,[33] together with the calculated values of 1.060 ± 0.082 eV (G3//B3LYP), 1.051 ± 0.085 eV (G3), 1.102 ± 0.20 eV (CBS-Q), 1.068 ± 0.092 (CBS-QB3), and 1.048 ± 0.090 eV (CBS-APNO). The theoretical values of Parthiban and Martin,[45] 1.080 ± 0.050 eV (W1) and 1.110 ± 0.040 eV (W2), are also included. These are complemented by the determinations of the relative gas-phase acidity of H_2O_2 by Ramond et al.,[35] in the form of the 298 K Gibbs energy for the reaction $H_2O_2 + C_2H^- \rightarrow HO_2^- + C_2H_2$ of −0.85 ± 0.48 kcal mol^{-1}, and by Bierbaum et al.,[34] measured as 298 K Gibbs energies of reaction $CF_3^- + H_2O_2 \rightarrow HO_2^- + CF_3H$ of −3.1 ± 1.8 kJ mol^{-1} ($0.7_4 \pm 0.4_3$ kcal mol^{-1}) and $F^- + H_2O_2 \rightarrow HO_2^- + HF$ of 12.3 ± 1.8 kJ mol^{-1} ($2.9_4 \pm 0.4_3$ kcal mol^{-1}). The network also contains the reaction enthalpy for $O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2$ of 4.6 ± 1.2 kcal mol^{-1} at 298 K of Fisher and Armentrout.[30] C(A)TN also contains the 0 K AE(HO_2^+/H_2O_2) of 15.112 ±0.035 eV by Litorja and Ruscic[31] as well as the presently refitted value of 15.095 ± 0.026 eV. (The inclusion or exclusion of either of these AE determinations were separately and extensively explored and tested, and the overall effect on the final value of the enthalpy of formation of HO_2 was found to be only 0.002 kcal mol^{-1}, attesting to the high "error tolerance" of the TN that is made possible by the redundancies in the TN which create robust, alternative roundabout routes.)

Included in the network are several high-quality theoretical atomization energies of HO_2 at 0 K, such as 165.84 ± 1.86 kcal mol^{-1} (G3//B3LYP), 165.62 ± 1.84 kcal mol^{-1} (G3), 165.81 ± 2.50 kcal mol^{-1} (CBS-Q), 166.93 ± 2.16 kcal mol^{-1} (CBS-QB3), 166.30 ± 1.50 kcal mol^{-1} (CBS-APNO), 165.27 ± 1.0 kcal mol^{-1} (CCSD(T)/CBS including corrections) from Dixon et al.,[74] 166.00 ± 0.15 kcal mol^{-1} from Flowers et al.,[46] and the HEAT value 694.56 ± 0.75 kJ mol^{-1} (166.00 ± 0.18 kcal mol^{-1}) of Tajti et al.,[75] together with the computed 0 K O−H bond dissociation energy of HO_2 of 42.3 ± 6 kcal mol^{-1} of Francisco et al.,[76] 47.81 ± 1.5 and 48.86 ± 2.5 kcal mol^{-1} of Jungkamp and Seinfeld,[77] and 48.02 ± 0.15 kcal mol^{-1} of Flowers et al.,[46] the computed 0 K O−O bond dissociation energies of HO_2 of 64.74 ± 1.5 and 63.57 ± 2.5 kcal mol^{-1} of Jungkamp and Seinfeld,[77] and 64.16 ± 0.15 kcal mol^{-1} of Flowers et al.,[46] the computed 0 K enthalpy of reaction $OH + O_2 \rightarrow HO_2 + O$ of 53.81 ± 0.15 kcal mol^{-1} of Flowers et al.,[46] as well as the computed 0 K O−H bond dissociation energies of H_2O_2 of 85.44 ± 1.5 and 87.87 ± 2.5 kcal mol^{-1} of Jungkamp and Seinfeld,[77] and the computed proton affinities of O_2 at 0 K of 100.48 ± 2.44 kcal mol^{-1} (G3//B3LYP), 101.31 ± 2.68 kcal mol^{-1} (G3), 99.26 ± 3.5 kcal mol^{-1} (CBS-Q), 98.99 ± 2.30 kcal mol^{-1} (CBS-QB3), and 100.58 ± 1.7 kcal mol^{-1} (CBS-APNO).

3.3.2. ATcT Enthalpies of Formation. The new value for the enthalpy of formation of HO_2 that is obtained by the ATcT approach using the C(A)TN that includes, inter alia, the various determinations discussed above, is $\Delta_f H_{298}°(HO_2) = 2.94 \pm 0.06$ kcal mol^{-1} and $\Delta_f H_0°(HO_2) = 3.64 \pm 0.06$ kcal mol^{-1}, where the quoted uncertainty corresponds to 95% confidence intervals (generally roughly equivalent to 2 std dev). This is the most accurate value for the enthalpy of formation of HO_2 available so far.

The value for $\Delta_f H°(HO_2)$ reported here is an additional and significant improvement over the interim ATcT value (3.06 ± 0.21 kcal mol^{-1} at 298 K and 3.76 ± 0.21 kcal mol^{-1} at 0 K), which was earlier privately communicated by us to Flowers et al.[46] and utilized by them as a benchmark for comparison with their very high-level theoretical evaluation. The interim value was based on the earlier version (1.022, significantly less extensive) of the C(A)TN. The current ATcT value for $\Delta_f H°(HO_2)$ is based on a TN that includes all available relevant knowledge. The theoretical value $\Delta_f H_{298}°(HO_2) = 2.96 \pm 0.10$ kcal mol^{-1} reported by Flowers et al.[46] is remarkably close to the current ATcT value of $\Delta_f H_{298}°(HO_2) = 2.94 \pm 0.06$ kcal mol^{-1}. While, as described above, the latter is based on inclusion of the atomization enthalpy and three reaction enthalpies reported by Flowers et al.,[46] it merits mentioning explicitly that exploratory ATcT solutions that excluded the high-level computational results of these authors led to an enthalpy of formation of HO_2 of 2.91 ± 0.09 kcal mol^{-1} at 298 K. Thus, the remaining knowledge in the TN produces a value that is extremely similar, and the inclusion of the computations of Flowers et al.[46] additionally enhances the knowledge content of the C(A)TN, further tightening the resulting uncertainty.[78]

The underlying ATcT statistical analysis, which utilizes the numerous redundancies in C(A)TN to reevaluate the initially reported or assigned uncertainties of the individual determinations, resulted overall in a significant number of adjustments: ∼13.5% of the initial uncertainties were found to be "optimistic" to at least some degree (and ∼10.7% needed to be augmented by 20% or more). Interestingly enough, in the section of the interdependency manifold directly relevant to HO_2 (spanned by the determinations described above), the preponderance of the reported/assigned uncertainties did not need to be readjusted, that is, practically all of the relevant determinations were, within their own uncertainties, consistent with the cumulative knowledge stored in the TN. The only significant (but not entirely unexpected, vide supra) exception to this overall consistency was the third-law Gibbs energy for $NO + HO_2 \rightarrow OH + NO_2$ obtained from Howard's[20] data, where the initially assigned uncertainty of ±0.4 kcal mol^{-1} needed to be expanded by a factor of nearly 4. At the same time, the ±0.3 kcal mol^{-1} uncertainty initially assigned to the second-law reaction enthalpy from the same data was found to be in complete harmony with the rest of the TN.

Of the other HO_2-related TN dependencies described above, only one more needed some adjustment, amounting to a moderate ∼30% augmentation of the estimated uncertainty of $\pm 0.4_3$ kcal/mol that was initially assigned by us to the older determination[34] of the gas-phase acidity of H_2O_2 relative to HF (the initially assigned uncertainty was based on the assumption that the underlying equilibrium constant is correct to within a factor of ∼2; the ATcT statistical analysis suggests a factor of ∼2.3). From the statistical viewpoint, having one uncertainty needing a modest correction and one needing a more serious correction within the relevant HO_2 manifold of dependencies is probably as good as one might have reasonably expected.[79]

The associated enthalpies of formation of the positive and negative ions of HO_2 (using the stationary electron convention) are $\Delta_f H_{298}°(HO_2^+) = 264.71 \pm 0.14$ kcal mol^{-1} (265.41 ± 0.14 kcal mol^{-1} at 0 K) and $\Delta_f H_0°(HO_2^-) = -21.86 \pm 0.11$ kcal mol^{-1} (−21.22 ± 0.11 kcal mol^{-1} at 0 K). The equivalent values using the thermal electron convention can be obtained by adding 2.5 kT to the positive ion enthalpy and subtracting the same amount for the negative ion.

The related proton affinity of molecular oxygen is $PA_{298}(O_2) = 100.98 \pm 0.14$ kcal mol^{-1} (99.81 ± 0.14 kcal mol^{-1} at 0 K). The Gibbs energy equivalent, the gas-phase basicity of O_2, is $GPB_{298}(O_2) = \Delta_{basic}G_{298}°(O_2) = -95.08 \pm 0.14$ kcal mol^{-1}. The gas-phase acidity of H_2O_2 is $GPA_{298}(H_2O_2) = \Delta_{acid}G_{298}°(H_2O_2) = 369.08 \pm 0.11$ kcal mol^{-1}, and the corresponding enthalpy of deprotonation of H_2O_2 is $\Delta_{acid}H_{298}°(H_2O_2) = 376.27 \pm 0.11$ kcal mol^{-1} (375.02 ± 0.11 kcal mol^{-1} at 0 K).

The O−H bond dissociation enthalpies of HO_2 and H_2O_2 are $BDE_{298}(H{-}O_2) = 49.16 \pm 0.06$ kcal mol^{-1} or $D_0(H{-}O_2) = 47.99 \pm 0.06$ kcal mol^{-1} and $BDE_{298}(H{-}O_2H) = 87.49 \pm 0.07$ kcal mol^{-1}, $D_0(H{-}O_2H) = 86.29 \pm 0.07$ kcal mol^{-1}. The O−O bond dissociation enthalpy of HO_2 is $BDE_{298}(HO{-}O) = 65.55 \pm 0.08$ kcal mol^{-1} or $D_0(HO{-}O) = 64.23 \pm 0.08$ kcal mol^{-1}.

The uncertainties for the reaction enthalpies given above have been obtained by standard error propagation methods from the related enthalpies of formation. Instead of standard uncertainty propagation, one should ideally use the full covariance matrix to estimate reaction enthalpies. While the latter is a common approach in select branches of science, this has virtually never been applied before in thermochemistry, largely because the traditional sequential approach is in most cases unable to produce the off-diagonal elements of the covariance matrix and, even if these were somehow estimated, there is no simple way of making a large covariance matrix available for day-to-day use of traditional thermochemical tables. The use of the full covariance matrix could produce, in cases where the enthalpies of the involved species are significantly cross-correlated, uncertainties for reaction enthalpies that are smaller.[8] While the full covariance matrix is also currently computed by ATcT, the present version of the ATcT Kernel does not yet exploit it to compute the uncertainties for reaction enthalpies. This, indeed, is one of the additional improvements that will be shortly implemented in the ATcT Kernel. Hence, for the moment, we resort to using the accepted standard error propagation method.

TABLE 2: Select Gas-phase Enthalpies of Formation and Enthalpies of Reactions from ATcT[a] (all in kcal mol^{-1})

species	$\Delta_f H°(0\ K)$ or $\Delta_r H°(0\ K)$	$\Delta_f H°(298.15\ K)$ or $\Delta_r H°(298.15\ K)$
HO_2	3.64 ± 0.06	2.94 ± 0.06
NO	21.64 ± 0.02	21.76 ± 0.02
ONO	8.79 ± 0.02	8.12 ± 0.02
OH	8.87 ± 0.03	8.93 ± 0.03
O	$58.997_1 \pm 0.000_5$	$59.567_2 \pm 0.000_5$
H_2O	−57.099 ± 0.007	−57.793 ± 0.007
H_2O_2	−31.01 ± 0.04	−32.45 ± 0.04
HO_2^+	265.41 ± 0.14	264.71 ± 0.14[b]
HO_2^-	−21.22 ± 0.10	−21.86 ± 0.10[b]
$NO + HO_2 \rightarrow ONO + OH$	−7.62 ± 0.07	−7.66 ± 0.07
$ONO \rightarrow NO + O$	71.85 ± 0.03	73.21 ± 0.03
$OH + HO_2 \rightarrow H_2O + O_2$	−69.61 ± 0.07	−69.66 ± 0.7
$H_2O_2 \rightarrow HO_2 + H$	86.29 ± 0.07	87.49 ± 0.07
$HO_2 \rightarrow OH + O$	64.23 ± 0.08	65.55 ± 0.08
$HO_2 \rightarrow H + O_2$	47.99 ± 0.06	49.16 ± 0.06
$O_2 + H^+ \rightarrow HO_2^+$	−99.81 ± 0.14	−100.98 ± 0.14[c]
$H_2O_2 \rightarrow HO_2^- + H^+$	375.02 ± 0.11	376.27 ± 0.11[d]

[a] All listed values have been obtained from Active Thermochemical Tables version 1.25 using the Core (Argonne) Thermochemical Network version 1.052 and are being reported here for the first time, except for O and H_2O, which were reported earlier,[6] based on the Core (Argonne) TN version 1.033. The quoted uncertainties for the enthalpies of formation are 95% confidence intervals. The quoted uncertainties for the reaction enthalpies have been obtained by simple standard error propagation of the 95% confidence limits of the involved species (see text for anticipated future use of the full covariance matrix via ATcT). [b] The listed values for the ions follow the stationary electron convention. To convert to 298 K values that conform to the thermal electron convention, *add* 1.481 kcal mol^{-1} (= 2.5 RT) to the 298 K enthalpy of formation of the *positive* ion and *subtract* the same amount for the *negative* ion. The 0 K values are the same in both conventions. [c] Proton affinity $PA_{298}(O_2) = 100.98 \pm 0.14$ kcal mol^{-1}; the corresponding gas-phase basicity $GPB_{298}(O_2) = \Delta_r G_{298}°(HO_2^+ \rightarrow O_2 + H^+) = 95.08 \pm 0.14$ kcal/mol. [d] Enthalpy of deprotonation $\Delta_{acid}H_{298}°(H_2O_2) = 376.27 \pm 0.11$ kcal/mol; the corresponding gas-phase acidity $\Delta_{acid}G_{298}°(H_2O_2) = 369.08 \pm 0.11$ kcal/mol.

All of the enthalpies of formation and reaction mentioned above are summarized in Table 2. This table also lists several other related thermochemical quantities obtained by the ATcT treatment of the same C(A)TN. Some of the listed values are related to the discussion of the $NO + HO_2 \rightarrow OH + NO_2$ equilibrium given below or are needed to complete the analysis of kinetic data in the companion paper.[9] Among these, a highly accurate value for the enthalpy of formation of OH is given, $\Delta_f H_{298}°(OH) = 8.93 \pm 0.03$ kcal mol^{-1} (8.87 ± 0.03 kcal mol^{-1} at 0 K). The ATcT value for OH fully confirms the revision of

Ruscic et al.,[59] where the new 298 K enthalpy of formation of 8.91 ± 0.07 kcal mol^{-1} (or 8.85 ± 0.07 kcal mol^{-1} at 0 K) was proposed based on conventional (sequential) thermochemical argumentation that combined new experiments and a critique of the original spectroscopic analysis that was the basis for the previous value, together with confirmatory state-of-the-art electronic structure computations. The new ATcT value differs from that of Ruscic et al.[59] only by 0.02 kcal/mol but is substantially more accurate. The enhanced accuracy is a direct result of the fact that ATcT can fully exploit *all* the available information simultaneously, including information that could not be conveniently used by Ruscic et al.[59] without obfuscating their argument.

The ATcT enthalpy of formation of H_2O_2, listed in Table 2, is closer to the value found in the Gurvich Tables[18,19] than that found in the JANAF Tables[10,11] and is more accurate than either of the two. The background surrounding the new ATcT values for OH and H_2O_2 involves complex argumentation that uses inter alia the new hypothesis testing ability of the ATcT approach and will be presented in a separate paper.[80]

Table 2 also provides new and accurate values for the enthalpies of formation of NO and NO_2, $\Delta_f H_{298}°(NO) = 21.76 \pm 0.02$ kcal mol^{-1} (21.64 ± 0.02 kcal mol^{-1} at 0 K), and NO_2, $\Delta_f H_{298}°(NO_2) = 8.12 \pm 0.02$ kcal mol^{-1} (8.79 ± 0.02 kcal mol^{-1} at 0 K). The improved accuracy of these species, which is part of the intricate manifold of C(A)TN interdependencies involving also other NO_x species, is again a direct result of the ATcT approach. Besides better utilization of the information, and the ability to easily introduce more recent information than that which was utilized in the JANAF Tables[10,11] or Gurvich Tables,[19] a crucial aspect of the general improvement of the resulting enthalpies of NO_x species is a consequence of the discovery of $D_0(N_2)$ as a "weak link" in the TN.[8,81] (The isolation of "weak links" in the TN is another capability newly introduced into the thermochemical field by the ATcT approach.) This prompted us to pursue a new experimental determination of the related threshold for $N_2 \rightarrow N^+ + N + e^-$ by photoionization.[81] The resulting improvement of the enthalpy of formation of the N atom in the gas phase (both the value and its uncertainty) propagates through NO into the NO_x manifold. While the complete discussion of principal NO_x species and the underlying dependencies will be given separately,[82] the truly relevant quantity in the context of the present work is the resulting bond dissociation energy of NO_2, rather than the individual values for the enthalpies of formation of NO and NO_2. This is true not only for the thermochemistry of $NO_2 \rightarrow NO + O$, but also for the $NO + HO_2 \rightarrow NO_2 + OH$ reaction. The enthalpy of the latter reaction is simply the difference between the HO−O and NO−O bond dissociation enthalpies, $\Delta_r H_T°(NO + HO_2 \rightarrow NO_2 + OH) = BDE_T(HO{-}O) - BDE_T(O{-}NO)$. Though the ATcT enthalpies of formation of NO and NO_2 are quite different than those found either in JANAF[10,11] or in Gurvich et al.[19] (which, incidentally, mutually disagree by more than their quoted uncertainties), the resulting value for BDE(O−NO) fortuitously does not change very much: $D_0(O{-}NO) = 71.9 \pm 0.2$ kcal mol^{-1} from JANAF,[10,11] $D_0(O{-}NO) = 71.84 \pm 0.16$ kcal mol^{-1} from Gurvich et al.,[19] and $D_0(O{-}NO) = 71.85 \pm 0.03$ kcal mol^{-1} from ATcT.

3.3.3. The ATcT Enthalpy and Gibbs Energy of the $NO + HO_2 \rightarrow NO_2 + OH$ Reaction. The current ATcT enthalpy for the reaction $NO + HO_2 \rightarrow NO_2 + OH$ is $\Delta_r H°(298.15\ K) = -7.65 \pm 0.07$ kcal mol^{-1} or $\Delta_r H°(0\ K) = -7.62 \pm 0.07$ kcal mol^{-1}. At 700 K, which is close to the central temperature of the overlapping temperature range between the forward and reverse as determined by Howard,[20] the ATcT value is $\Delta_r H°(700\ K) = -7.38 \pm 0.07$ kcal mol^{-1}, to be compared to Howard's second-law value of −7.2 ± 0.3 kcal mol^{-1}. Therefore, once again, it may be concluded that the slope of the van't Hoff plot of Howard's data is, in fact, correct, at least within its own uncertainty.

However, the ATcT value for the related Gibbs energy of this reaction at 700 K is $\Delta_r G°(700\ K) = -5.12 \pm 0.07$ kcal mol^{-1} or $K_{Eq}(700\ K) = 40 \pm 2$. The equilibrium constant from Howard's data at 700 K is 20 ± 6, that is, a factor of 2 smaller. This ATcT result is quite firm and verifies the conclusion that was obtained earlier (vide supra) from the internal consistency analysis of Howard's data.

In addition, the statistical analysis of the C(A)TN that occurs as part of the ATcT procedure suggests that the initially assigned uncertainty of the third-law Gibbs energy from Howard's data[20] should be augmented by a factor of ∼4 (vide supra). This in turn implies that the absolute value of the equilibrium constant of Howard[20] would need to be increased by at least 70−80% before it becomes marginally harmonious with the remaining knowledge stored in the TN.

Hence, an internal consistency analysis of Howard's[20] equilibrium constant of $NO + HO_2 \rightarrow NO_2 + OH$, the juxtaposition of Howard's third-law Gibbs energy to the cumulative thermochemical knowledge existing in the C(A)TN, and the final ATcT enthalpies of formation, all produce the same conclusion: the related equilibrium constant is too low by a factor of ∼2. Barring even more complex scenarios, which conceivably could call into question both the forward and reverse rates, these analyses suggest that either the rate constant for $NO + HO_2$ measured by Howard[20] is too low by a factor of ∼2 or the $OH + NO_2$ rate constant is too high by a similar factor. Thermochemistry alone cannot provide further guidance in narrowing down the alternatives. However, since the $NO + HO_2$ reaction is of major importance in stratospheric ozone depletion,[83] its rate constant[84−89] and temperature dependence[20,88] have been measured a number of times. All these studies are in remarkable agreement, thus pointing toward the rate constant of the reverse reaction, $OH + NO_2$, as the likely source of the problem. This conclusion provides the spriritus movens for the kinetic measurements reported in the companion study,[9] which indicate that the rate for $NO_2 + OH$ is indeed smaller by a factor of 2 than that measured by Howard.[20]

It should be emphasized at this point that the thermochemical values reported here are independent from the results of the companion kinetic study[9] and vice versa. The primary goal of the companion kinetic study is to provide a new measurement of the suspected kinetic rate for $NO_2 + OH$ and hence explicitly explore one of the consequences of the present thermochemical study. While the companion kinetic study utilizes ATcT thermochemistry to evaluate several equilibrium constants that enter in the overall reaction mechanism, these back reactions have a negligible influence on the measured rates and are included essentially for the sake of completeness. In addition to evaluating the back reactions, the companion kinetic study uses the ATcT thermochemistry to perform a *post factum* comparison between the newly determined rate constant for $NO_2 + OH$ to the transformed (and extrapolated) rate constant obtained from the literature values of the $NO + HO_2$ rate constant and the ATcT equilibrium constant. Hence, the reported k_{NO_2+OH} is for all practical purposes independent of ATcT thermochemistry and can be, at least in principle, used to possibly further enhance the ATcT thermochemistry. Howard's[20]

k_{NO+HO_2} and k_{NO_2+OH} from the companion kinetic study[9] overlap in the rather short range centered at ~1250 K. The shortness of the range frustrates an attempt to extract a second-law value for the reaction enthalpy but yields a third-law Gibbs energy $\Delta_r G_{1250}°(NO + HO_2 \rightarrow OH + NO_2) = -3.48 \pm 0.75$ kcal/mol (which compares excellently to the ATcT value for the Gibbs energy at 1250 K of -3.41 ± 0.06 kcal/mol). Since this new third-law value coincides with the ATcT value to within 0.1 kcal/mol, and has an overall uncertainty that is more than 1 order of magnitude larger than the ATcT value, its propensity to further influence the already very accurate ATcT thermochemistry is marginal. As a final touch to the thermochemical portion of the combined studies, we have explicitly evaluated this aspect and verified that the resulting thermochemical values (and their uncertainties) stay unchanged upon inclusion of the new third-law into the C(A)TN, with differences being less than 0.001 kcal/mol.

4. Conclusions

Through the use of the ATcT approach, the best currently available value for the enthalpy of formation of HO_2 has been obtained, together with the related enthalpies of formation of its positive and negative ions and several related bond energies, such as the O−H bond dissociation enthalpy of H_2O_2 and O−H and O−O bond dissociation enthalpies of HO_2 (see Table 2).

The new thermochemistry for HO_2 and other related species, such as OH, NO, and NO_2, as well as other arguments based on an analysis of internal consistency and external consistency with the cumulative knowledge existing in the Thermochemical Network, strongly suggest that the previous equilibrium constant for $NO + HO_2 \rightarrow NO_2 + OH$ was underestimated by a factor of ~2, implicating that the $OH + NO_2$ rate was overestimated by the same factor.

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(78) For the purpose of comparison, if *only* the four computational determinations of Flowers et al.[46] that were inserted in C(A)TN are used in a small localized TN together with initially assigned individual uncertainties of ± 0.15 kcal mol^{-1}, and one uses ATcT to analyze and solve the localized TN, then the theoretical value of 2.96 ± 0.12 kcal mol^{-1} is obtained.

(79) If *all* of the initial uncertainties (as originally reported or as reevaluated during the critical data analysis step that occurs prior to inserting the determination into the TN) were indeed 95% uncertainty intervals, then the ATcT statistical analysis would generally find that ∼95% of the uncertainties are large enough to completely contain the difference between the measured quantity and the same quantity as recalculated from the final ATcT enthalpies (i.e., the "error" of the original determination), while ∼5% of the uncertainties would not be sufficiently large to contain this difference. The ∼5% set of uncertainties would be composed roughly as follows: ∼3% of uncertainties would be able to contain the "error" if they were augmented by 20% or less, ∼1.6% would need to be augmented by 20−50%, ∼0.4% would need to be augmented between 50 and 100%, and about 0.02% would need to be augmented by a factor between 2 and 4. Corrections larger than a factor of 4 would be exceedingly rare. Such ideal behavior almost never takes place in practice, attesting to the fact that a significant fraction of uncertainties reported in the literature are "optimistic". In fact, from the number of "optimistic" uncertainties uncovered and corrected within the global ATcT analysis of the ∼6400 determinations present in the current version of C(A)TN, one obtains a hint that the *average* initial uncertainty (many of which have been already expanded during the critical evaluation step above the originally reported size by a significant factor) roughly corresponds only to an ∼86% confidence interval (approximately equivalent to 1.5 std dev, as opposed to the desired coverage factor of ∼2 std dev). Constructing the network using the uncorrected uncertainties (as claimed in the original literature) would have resulted in a substantially higher percentage of "optimistic" uncertainties. The picture is even murkier once the underlying distribution is examined in more detail: a substantial fraction of the "optimistic" uncertainties correspond to high-magnitude outliers, far beyond the statistical expectation. Some of these probably correspond to hidden systematic errors. The unusual ability of the TN approach of ATcT to uncover at least some of these systematic errors will be discussed in future publications on ATcT.

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