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Thermochemistry of Methyl and Ethyl Nitro, RNO_2, and Nitrite, RONO, Organic Compounds[†]

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Computational quantum theory is employed to determine the thermochemical properties of *n*-alkyl nitro and nitrite compounds: methyl and ethyl nitrites, CH_3ONO and C_2H_5ONO, plus nitromethane and nitroethane, CH_3NO_2 and $C_2H_5NO_2$, at 298.15 K using multilevel G3, CBS-QB3, and CBS-APNO composite methods employing both atomization and isodesmic reaction analysis. Structures and enthalpies of the corresponding *aci*-tautomers are also determined. The enthalpies of formation for the most stable conformers of methyl and ethyl nitrites at 298 K are determined to be -15.64 ± 0.10 kcal mol^{-1} (-65.44 ± 0.42 kJ mol^{-1}) and -23.58 ± 0.12 kcal mol^{-1} (-98.32 ± 0.58 kJ mol^{-1}), respectively. $\Delta_f H^o$(298 K) of nitroalkanes are correspondingly evaluated at -17.67 ± 0.27 kcal mol^{-1} (-74.1 ± 1.12 kJ mol^{-1}) and -25.06 ± 0.07 kcal mol^{-1} (-121.2 ± 0.29 kJ mol^{-1}) for CH_3NO_2 and $C_2H_5NO_2$. Enthalpies of formation for the *aci*-tautomers are calculated as -3.45 ± 0.44 kcal mol^{-1} (-14.43 ± 0.11 kJ mol^{-1}) for *aci*-nitromethane and -14.25 ± 0.44 kcal mol^{-1} (-59.95 ± 1.84 kJ mol^{-1}) for the *aci*-nitroethane isomers, respectively. Data are evaluated against experimental and computational values in the literature with recommendations. A set of thermal correction parameters to atomic (H, C, N, O) enthalpies at 0 K is developed, to enable a direct calculation of species enthalpy of formation at 298.15 K, using atomization reaction and computation outputs.

I. Introduction

Accurate formation enthalpies, $\Delta_f H^o{}_{298}$, for the simplest nitro and nitrite molecules are required in order to understand reaction paths and assist in the development of detailed chemical kinetic mechanisms which can be applied to model the formation and destruction of nitrogen species in a variety of environments, particularly for atmospheric and combustion chemistries. Since less than 0.02% of known organic species have had their heats of formation measured[2] the application of quantum chemistry methods for this data is of value, provided that reasonable accuracy can be obtained. The establishment of these values will also aid in the determination of the thermochemical properties of higher homologues via use of isodesmic reactions with group conservation (isogeitonic reactions). This study continues development and evaluation of thermochemical properties on nitrates from our previous analysis on the thermochemistry of HONO isomers.[1]

Nitro (RNO_2) and nitrite (RONO) derivatives of hydrocarbons undergo thermal decomposition at relatively low temperatures and hence have potential as both propellants and energetic materials (The alkylnitro ($R-NO_2$) and nitrite (RO−NO) bond-cleavage reaction barriers are only 61 and 40 kcal mol^{-1}, respectively).[3−7] Nitro compounds have been widely studied by experimental and theoretical methods;[3−29] however, the thermochemical data are surprisingly limited. Available data on enthalpies of formation of related systems including some isomers of methyl and ethyl homologues are collected in Table 1. The data are often scattered, in some cases substantially, and they are sometimes even controversial.

As can be seen, ethyl nitrite ($\Delta_f H^o{}_{298} = -25.9$ kcal mol^{-1}) is reported to be more stable than nitroethane ($\Delta_f H^o{}_{298} = -23$ to -24 kcal mol^{-1}) according to the NIST database.[30] Note that the experimental conclusion for ethyl nitrite is based on a single determination derived from a kinetic analysis of the decomposition of diethyl peroxide in the presence of NO in 1952.[25] In contrast, the nitrite isomer of the simplest nitro compound, HONO, is more stable than its nitryl form HNO_2.[1] Recently, we have reported our computations on $\Delta_f H^o{}_{298}$ of nitrous acid isomers and have estimated this difference as 8 kcal mol^{-1} in favor of the *trans*-nitrite isomer.[1] Our recommended values for heats of formation were based on the thermochemical analysis of several isodesmic reactions and the average values from CBS-APNO, G3, and CBS-QB3 calculations.

Nitromethane (CH_3NO_2, $MeNO_2$) has been studied more extensively, and it has repeatedly been included in computational chemistry test sets, such as the popular G2/97,[29] in order to validate theoretical schemes. The heat of formation of CH_3NO_2 in the paper outlining the CBS-QB3 method for example is reported as -17.8 ± 0.1 kcal mol^{-1}[31] while CH_3ONO, from the same article, has an enthalpy of formation of -15.8 ± 0.02 kcal mol^{-1}.

Decomposition of the simplest nitro alkanes as prototype models for larger monopropellants has been the subject of numerous studies.[1,3−13,17−22] According to Dewar et al.,[5] the preferred pathway for nitromethane decomposition is the

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[†] Part 1: Thermochemistry of Nitrous Acid Isomers (R ≡ H). See ref 1.

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TABLE 1: Reference Formation Enthalpies for Species[a] (kcal mol^{-1})

species	experimental data	calculated data
NO	**21.76**,[39] 21.58[30]	22.3[40b]
NO_2	**8.12**,[39] 7.91[30]	
HNO	**25.6**,[46] 23.8[30]	23.20,[35] 25.41,[3] 26.1[40b]
trans-HONO	−**18.87**,[42]−18.84[43] −17.68 ± 1.00[35]	−18.33,[44] −18.59[3] −**18.90** ± 0.05[1]
cis-HONO	−18.3,[33] −**18.34**[43]−18.51[42]	−**18.40** ± 0.05,[1] −19.11 ± 1.12 [33]
HNO_2		−**10.90** ± 0.05,[1] −14.15 ± 1.4[35]
$HONO_2$	−**32.10**[30]	−32.15[22]
CH_3ONO	−**15.64** ± 0.20[30] −15.79 ± 0.25,[41] −15.3[45] −16.8 ± 0.8,[41] −15.87 ± 0.23[49] −14.93 ± 0.26,[30] −15.6[33]	−15.64; this work
CH_3NO_2	−19.30 ± 0.3,[30] −17.86 ± 0.15[41] −17.8 ± 0.2,[48] −17.9,[29] −17.85[47] −17.75 ± 0.11,[49] 13.6 ± 0.3[41]	−**17.67**; this work −16.5[8c]
C_2H_5ONO	−25.9[25]	−23.58; this work
$C_2H_5NO_2$	−**24.38** ± 0.3,[41] −24.45 ± 0.15[49] −23.53 ± 0.35,[41] −22.7 ± 0.3[41] −24.81[51a]	−25.06; this work −24.5 ± 1[d12]
C_2H_6	−**20.04**[30]	
C_3H_8	−**25.02**,[30] −24.83[30]	
CH_3OH	−**48.0**[30]	
C_2H_5OH	−**56.23** ± 0.12[30]	
CH_3OCH_3	−**43.99** ± 0.12[30]	
	$\Delta_f H^o$(298 K)	Experimental Integrated Heat Capacity of Atoms T_c'(A)[e]
H	**52.103**[30]	1.4811[47a,60]
O	**59.555,**[30] 59.567[39]	1.6075[47a,60]
C	**171.29**[30]	1.5621[47a,60]
N	**112.97**[30]	1.4811[47a,60]
	$\Delta_f H^o$(0 K)	Experimental Elemental Heat Corrections T_c(A)[f]
H	**51.63**±0.001[50]	1.012[47a,50]
O	**58.99** ± 0.02[50]	1.037[47a,50]
C	**170.11** ± 0.1;[64] 169.98 ± 0.1[50]	0.25 [g47a,50]
N	**112.53** ± 0.02[50]	1.036[47a,50]

[a] Data in bold used in evaluations. [b] On the basis of average BDEs. [c] CCSD(T)/aug-cc-pVnZ. [d] DFT result. [e] Integrated heat capacity ($\Delta H'_T = H_{298} - H_0$). [f] Derived from corresponding elements ($\Delta H_T = H_{298} - H_0$) in standard state (gas-phase H_2,N_2, and O_2). [g] For graphite.

rearrangement to methyl nitrite, CH_3ONO, followed by the concerted elimination of nitroxyl to form HNO + $CH_2{=}O$. The simple dissociation reaction to $^{\bullet}CH_3$ + $^{\bullet}NO_2$ radicals and the intermolecular transfer of oxygen, which is reported to be favored in detonating shock waves, are alternative pathways.[6] The principal carbon-containing products from thermal decomposition of supercritical CH_3NO_2 at liquid-like densities are reported by Brower et al.[7] to be HCN and CO_2 whereas at low pressures CH_4 and CO were found to dominate. Brower et al. also report at final nitrogen products from the supercritical decomposition of CH_3NO_2 as N_2O + NO, in contrast to the reported rearrangement mechanism of Dewar[6] which leads to HNO. Here the fate of N-containing products at lower pressures is not considered explicitly. The activation energy for pyrolysis at higher density (0.6 g/cm^3) was estimated as 40.63 kcal mol^{-1}.

The low-density pyrolysis is thought to occur by an initial C−N bond rupture whose bond dissociation enthalpy can be estimated *via*:

$$D(H_3C{-}NO_2) = \Delta_f H^\circ_{298}(^{\bullet}CH_3) + \Delta_f H^\circ_{298}(^{\bullet}NO_2) - \Delta_f H^\circ_{298}(CH_3NO_2)$$

$$= 35.06 + 7.91 - (-17.86) = 60.83 \text{ kcal mol}^{-1}$$

and the use of $\Delta_f H^\circ_{298}(NM) = -17.86$ kcal mol^{-1}.[41] Alternately, a value of 60.59 kcal mol^{-1} is obtained using $\Delta_f H^\circ_{298}(^{\bullet}CH_3) = 34.82$ kcal mol^{-1} as recommended by Chase.[30]

This is in agreement with the activation energy, E_a, determined for the overall decomposition process in the earliest (1935) experiments on nitromethane[21] of 61 kcal mol^{-1} where the reaction $CH_3NO_2 \rightarrow CH_3NO + {}^1/_2O_2$ was postulated to be the primary step. We note that the authors reported that nitrosomethane was not detected and postulated that it was unstable, rapidly isomerizing to formaldoxime, $CH_2{=}NOH$. Both oxygen atom detachment and C−H bond cleavage from nitromethane require significant energies, 96 and 101 kcal mol^{-1}, respectively at CBS-QB3 level (*vide infra*), whereas its decomposition to methoxy and NO fragments has a much lower dissociation enthalpy $\Delta H_{rxn}(298)$ at 41.7 kcal mol^{-1}.

Rearrangement of nitromethane to corresponding nitrite, $CH_3NO_2 \rightarrow CH_3ONO$, is competitive with direct C−N bond rupture according to experiment[19] as well as being in agreement with Dewar's conclusions based on semiempirical MINDO/3 calculations.[5] Higher level calculations predict the opposite preference; *viz.*, *C*−NO_2 bond cleavage is favored.[9,10] The barrier of the rearrangement determined by infrared multiple-photon dissociation is 55.5 kcal mol^{-1}, which is comparable to the C−N bond energy in nitromethane of 59.4 kcal mol^{-1}.[32]

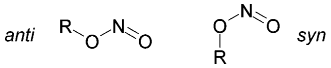
Early *ab initio* calculations at MP2/6-31G(d) level of theory by McKee[9] reported the unimolecular rearrangement barrier of CH_3NO_2 to CH_3ONO to be 73.5 kcal mol^{-1}, some 16.1 higher than the C−N bond energy in CH_3NO_2 (57.4 kcal mol^{-1}). The transition state was found to be loose with a weak interaction between the NO_2 and CH_3 fragments. Here, the cleaving C−N and the forming C−O bonds are far from their equilibrium distances at 3.2 Å and 3.7 Å, respectively. In the further work of McKee[10] using multireference calculations (MRCI/6-3lG*//

CAS/6-3lG(d)) the rearrangement barrier was reduced to 70 kcal mol^{-1}, only 10 kcal mol^{-1} above the sum of $^{\bullet}CH_3$ and $^{\bullet}NO_2$ product enthalpies. This value is still in conflict with experiment where the unimolecular rearrangement is observed. High level *ab initio* methods predict an activation barrier for rearrangement that is higher than the dissociation energy to $^{\bullet}CH_3$ and $^{\bullet}NO_2$ radicals while the experimental work of Lee and co-workers[19] suggests that it is lower. Brower has reported evidence indicating a shift from homolysis at low pressures to rearrangement in dielectric media.[7]

For nitroethane, the concerted elimination of HONO *via* a five-centered intermediate is the lowest energy decomposition channel according to the BAC-MP4 [35b] and B3LYP/6-311+G(3df,2p) calculations.[12] Estimated DFT barriers for nitroethane and 2-nitropropane of 42.0 and 39.2 kcal mol$^{-1,}$ respectively are comparable to the experimental activation energy data of Benson and co-workers of 43.0 and 42.0 kcal mol^{-1}.[22]

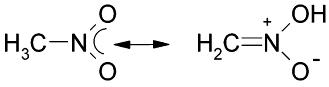
In studies on the detonation of liquid nitromethane and methyl nitrite it has been shown from collaborative CCSD(T)/6-311++G(2d,2p) computations that the corresponding anions have lower fragmentation energies than their neutral precursors.[13] Dissociation of the NM anion to $CH_3^{\bullet}$ radical and NO_2^- ion requires only 18.7 kcal mol^{-1} of energy. The adiabatic curve of the triplet state decomposition of nitromethane through C−N bond also exhibits a lower energy barrier of 33 kcal mol^{-1}, as determined by MCSCF method.[11]

Syn−*anti* equilibrium and conformations of alkyl nitro compounds have been studied by several researchers.[9,15,26] These results show that R-groups mainly destabilize the sterically favored *syn* conformer.



The magnitude of the steric forces has been shown to correlate with data from ^1H NMR on relative stabilities on primary alkyl nitrites.[26] For isoalkyl nitrites, the reverse order was obtained as was expected. Theoretical models also confirm the stability of *syn* conformers.[9,15]

Other, less studied, isomers of alkyl - NO_2 derivatives are the *aci*-forms of corresponding nitroalkanes−nitronic acids. The *aci*-forms are reported to play an important role in photochemical processes and in pyrolysis[9,16,20] and references cited therein. The barrier for the thermally forbidden 1,3-H transfer in nitro ↔ *aci*-nitro rearrangement is as high as 61.57 kcal mol^{-1} predicted at B3LYP/6-31G(d,p) level and 63.50 kcal mol^{-1} at the CBS-QB3 level [our unpublished data]. This is in accordance with the results of Khrapkovskii and co-workers predicting 61.7 kcal mol^{-1} within the B3LYP/6-311++G(df,p) approximation.[17a]



The MP2/6-31G(d) result of McKee[9] is somewhat higher at 75 kcal mol^{-1} The native form of nitromethane has been estimated at the MP2 level, as being 21.8 kcal mol^{-1} more stable than the *aci*-form,[9] while Lammertsma and Prasad estimated this difference to be 14.1 kcal mol^{-1} using the G1 composite method.[16] G2MP2//B3LYP/6-311++G(2d,2p) predicts the similar difference value of 14.7 kcal mol^{-1}.

In the present work, we have evaluated the formation enthalpies of simple *n*-alkyl nitro compounds bearing −ONO (nitrite) and $-NO_2$ (nitro-) moieties on the basis of their most stable conformers as well as *aci*-form tautomers, using multilevel computational methods. We used both complete basis set and Gaussian multilevel method calculations. The methods employ a variety of different geometries, frequency determinations and higher order energy corrections (*vide infra*). The accuracy of these methods has been demonstrated in our previous study on HONO isomers.[1]

We evaluate and critically analyze enthalpies the of following *n*-alkyl derivatives: nitromethane (CH_3NO_2, $MeNO_2$) and nitroethane ($C_2H_5NO_2$, $EtNO_2$), including their *aci*-form tautomers: methane nitronic acid, $CH_2N(O)OH$, and ethane nitronic acid, $CH_3CHN(O)OH$, as well as methyl nitrite (CH_3ONO, MeONO), and ethyl nitrite or nitrous acid ethyl ester (C_2H_5-ONO, EtONO).

II. Computation Methods

The relative stability of RONO and RNO_2 systems, the homolytic bond dissociation energies and the heats of formations determined from radical and molecule work reactions are evaluated with the *ab initio* and DFT-based multilevel schemes G3,[36] CBS-QB3,[31] and CBS-APNO[37] as implemented in the Gaussian 03[38] suite of programs.

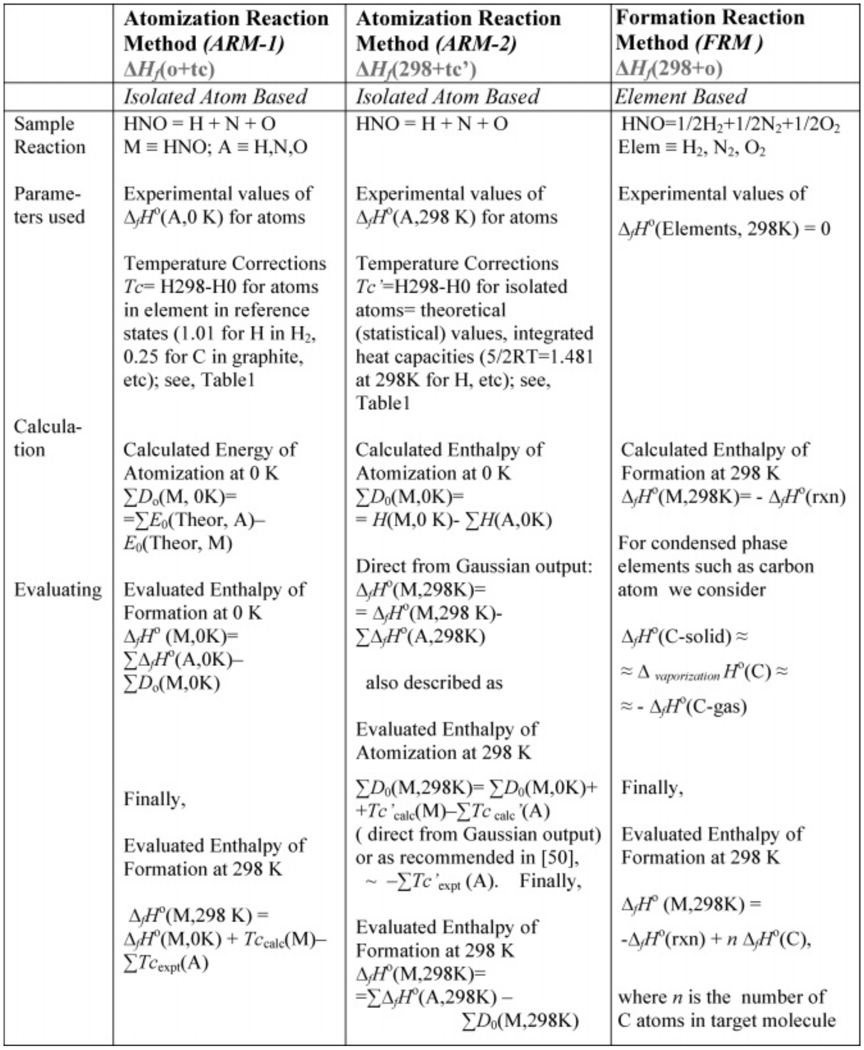
The complete basis set extrapolation method of Petersson and co-workers[48] using an atomic pair natural orbital basis set, CBS-APNO, is our highest-level method. The calculation includes a HF/6-311G(d,p) geometry optimization to obtain the enthalpy and free energy corrections, with final geometry reoptimized at QCISD/6-311G(d,p) level of theory. This QCISD geometry is then used in single point calculations at the QCISD(T), MP2-(Full), HF, and MP2 levels. The CBS extrapolation included in the last step computes the final energies.

CBS-QB3 is a more reasonable time-expense complete basis method. Geometries and frequencies are calculated at B3LYP/6-311G(2d,d,p) level. Two additional calculations are used to approximate higher order of contributions: MP4(SDQ)/6-31+G-(d(f),p) and CCSD(T)/6-31+G†. In place of quadratic configuration interaction QCISD(T) used in CBS-APNO (as well as in the G3 below), the coupled cluster singles and doubles with perturbative triples CCSD(T) is used, which is considered to improve accuracy over the QCISD(T) method especially for spin contaminated radicals.[29,31] Correction for spin contamination (proportional to $\langle S^2\rangle$) and size-consistent higher order empirical correction are also incorporated. This method is attractive for further use in the evaluation of larger homologues, due to its reasonable time expenditure.

Equilibrium structures and thermal corrections in G3 method are based on HF/6-31G(d) calculations. The G3 protocol[36] begins with a HF/6-31G(d) geometry optimization and a frequency calculation, with the frequencies scaled by 0.8929. The next step is a reoptimization of geometry at MP2(Full)/6-311G(d) level. The improved MP2 geometry then used for a series of single point calculations to account for electronic correlation effects at the QCISD(T,E4T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3large levels. Corrections are also applied to estimate the effect of diffuse and higher polarization functions at the MP4 level, and a correction for correlation effects beyond MP4 using quadratic configuration interaction.

All values reported in this paper are for a standard state of 298.15 K and 1 atm unless otherwise stated. The absence of imaginary frequencies verified that all stable structures were true minima at their respective levels of theory. Transition states have been characterized with only one negative eigenvalue in the force constant (Hessian) matrices.

TABLE 2: Description of Different Calculation Schemes[a] for Enthalpy of Formation $\Delta_f H^\circ_{298}$



	Atomization Reaction Method *(ARM-1)* ΔH_f(o+tc)	**Atomization Reaction Method *(ARM-2)*** ΔH_f(298+tc')	**Formation Reaction Method *(FRM)*** ΔH_f(298+o)
	Isolated Atom Based	*Isolated Atom Based*	*Element Based*
Sample Reaction	HNO = H + N + O M ≡ HNO; A ≡ H,N,O	HNO = H + N + O	HNO=1/2H_2+1/2N_2+1/2O_2 Elem ≡ H_2, N_2, O_2
Parameters used	Experimental values of $\Delta_f H^o$(A,0 K) for atoms Temperature Corrections *Tc*= H298-H0 for atoms in element in reference states (1.01 for H in H_2, 0.25 for C in graphite, etc); see, Table1	Experimental values of $\Delta_f H^o$(A,298 K) for atoms Temperature Corrections *Tc'*=H298-H0 for isolated atoms= theoretical (statistical) values, integrated heat capacities (5/2RT=1.481 at 298K for H, etc); see, Table1	Experimental values of $\Delta_f H^o$(Elements, 298K) = 0
Calculation	Calculated Energy of Atomization at 0 K $\sum D_o$(M, 0K)= =$\sum E_0$(Theor, A)– E_0(Theor, M)	Calculated Enthalpy of Atomization at 0 K $\sum D_0$(M,0K)= = *H*(M,0 K)- $\sum H$(A,0K) Direct from Gaussian output: $\Delta_f H^o$(M,298K)= = $\Delta_f H^o$(M,298 K)- $\sum \Delta_f H^o$(A,298K)	Calculated Enthalpy of Formation at 298 K $\Delta_f H^o$(M,298K)= - $\Delta_f H^o$(rxn) For condensed phase elements such as carbon atom we consider
Evaluating	Evaluated Enthalpy of Formation at 0 K $\Delta_f H^o$ (M,0K)= $\sum \Delta_f H^o$(A,0K)– $\sum D_o$(M,0K) Finally, Evaluated Enthalpy of Formation at 298 K $\Delta_f H^o$(M,298 K) = $\Delta_f H^o$(M,0K) + Tc_{calc}(M)– $\sum Tc_{expt}$(A)	also described as Evaluated Enthalpy of Atomization at 298 K $\sum D_0$(M,298K)= $\sum D_0$(M,0K)+ +Tc'_{calc}(M)–$\sum Tc_{calc}'$(A) (direct from Gaussian output) or as recommended in [50], ~ –$\sum Tc'_{expt}$ (A). Finally, Evaluated Enthalpy of Formation at 298 K $\Delta_f H^o$(M,298K)= =$\sum \Delta_f H^o$(A,298K) – $\sum D_0$(M,298K)	$\Delta_f H^o$(C-solid) ≈ ≈ $\Delta_{vaporization} H^o$(C) ≈ ≈ - $\Delta_f H^o$(C-gas) Finally, Evaluated Enthalpy of Formation at 298 K $\Delta_f H^o$ (M,298K) = -$\Delta_f H^o$(rxn) + *n* $\Delta_f H^o$(C), where *n* is the number of C atoms in target molecule

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[a] See Appendix for details.

Two atomization and a formation work reaction schemes (see Table 2 and the Appendix for details) and the isodesmic reaction analysis are used to determine enthalpies of formation at 298.15 K.

III. Results and Discussion

Enthalpies of formation of the title compounds are determined using two atomization work reaction schemes and by isodesmic work reaction schemes. We consider the final enthalpies from the isodesmic reaction analysis as the more accurate data because of the cancellation of residual computational errors. Table 1 lists available experimental values and our evaluated data for the $\Delta H_f^o{}_{298}$ of reference compounds used in the isodesmic reaction analysis. Comparative results of this analysis are presented in Table 3 and 4 and are discussed in section III.1.

Heats of formation for target compounds calculated by two atomization (ARM -1 and ARM-2) and a formation reaction (FRM) methods are listed in Table 6 and are detailed in sections III.2 and III.3 and the Appendix. Bond energies are tabulated in Tables 7 −9 and critically analyzed in section III.4.

In general, the enthalpies of formation determined by two atomization reaction schemes are in very good agreement with the available experimental data and our recommended values from the isodesmic reaction analysis.

TABLE 3: Calculated $\Delta_f H^\circ$/kcal Mol^{-1} of Nitromethane and Methyl Nitrite Using Work Reactions

	CH_3NO_2			
species	reacn 1	reacn 3	reacn 4	*cis*-CH_3ONO reacn 2[a]
CBS-QB3	−18.01	−17.51	−17.75	−15.54
CBS-APNO	−17.13	−17.66	−17.48	−15.64
G3	−17.96	−17.81	−17.70	−15.74
mean	−17.67 ± 0.27			−15.64 ± 0.10
experiment	−17.86 ± 0.15[41] −19.3 ± 0.3[51]			−15.64 ± 0.2[30]

[a] The *cis* form is the most stable isomer of CH_3ONO and is used for evaluations—see text.

III.1. $\Delta_f H^o{}_{298}$ from Isodesmic Work Reactions. A number of isodesmic work reactions were employed in this procedure with the chemistry (structures) of reactants and products closely matched in order to benefit from the cancellation of errors, which are inherent in nonexact quantum mechanical calculations.

Methyl Nitrite and Nitromethane. The enthalpies for methyl-derivatives at 298 K were calculated using thermochemical data for nitric acid and two nitrous acid isomers—HNO_2 and HONO-*cis* (reactions 1−3) together with well-

TABLE 4: Calculated $\Delta_f H°$/kcal Mol^{-1} of Nitroethane and Ethyl Nitrite Using Work Reactions

	$C_2H_5NO_2$		*cis*−*trans*-C_2H_5ONO	
species	reacn 5	reacn 6	reacn 7	reacn 8[a]
CBS-QB3	−25.05	−25.14	−23.49	−23.54
CBS-APNO	−25.01	−25.15	−23.45	−23.55
G3	−25.00	−25.01	−23.74	−23.70
mean	−25.06 ± 0.07		−23.58 ± 0.12	
B3LYP/6-31G(d,p)	−25.19	−24.81	−23.20	−22.77
CBSB7	−25.59	−24.82	−23.20	−22.88
experiment	−24.38 ± 0.3[41] −23.53 ± 0.35[41] −22.7 ± 0.3[41]		−25.9[25]	

[a] The c*is*−*trans* conformer is the most stable isomer of C_2H_5ONO and is used for evaluations—see text.

TABLE 5: Formation Enthalpies for *aci*-Species (kcal mol^{-1})

species	reacn 9 $CH_2{=}N(O)OH$	reacn 10 $CH_3CH{=}N(O)OH$
CBS-QB3	−3.95	−13.75
CBS-APNO	−3.13	−14.57
G3	−3.27	−14.43
mean	−3.45 ± 0.44	−14.25 ± 0.44

established reference compounds such as ethane, dimethyl ether, ..., *etc.* as shown in Table 1:

$$CH_3CH_3 + HONO_2 \leftrightarrow \mathbf{CH_3NO_2} + CH_3OH \quad (1)$$

$$CH_3OCH_3 + HONO\text{-}cis \leftrightarrow \mathbf{CH_3ONO\text{-}\mathit{cis}} + CH_3OH \quad (2)$$

$$CH_3OCH_3 + HNO_2 \leftrightarrow \mathbf{CH_3NO_2} + CH_3OH \quad (3)$$

Reaction 2 was used to determine a formation enthalpy for methyl nitrite of −15.64 ± 0.10 kcal mol^{-1}, which is in excellent agreement with an experimental value of −15.64 ± 0.20 kcal mol^{-1},[43] Table 3. This result was then used *via* isomerization reaction 4 for nitro to nitrite isomers (Figure 1)

$$CH_3NO_2 \leftrightarrow \mathbf{CH_3ONO\text{-}\mathit{cis}} \quad (4)$$

to additionally determine a value for nitromethane.

The final heat of formation for nitromethane, averaged over all three multilevel computations from reactions 1, 3, and 4, of −17.67 ± 0.27 kcal mol^{-1}, is in very good agreement with the experimentally determined value of −17.86 ± 0.15 kcal mol^{-1}.[41] It differs considerably from the more recent value by Knobel et al.[51b] of −19.3 ± 0.3 kcal mol^{-1} (Table 3). The data presented here on nitromethane are dependent on our previously reported values for HONO and HNO_2,[1] and we feel this provide support and validation for our complete data set.

The range in the calculated $\Delta_f H^o$ values across the work reactions used for nitromethane is only 0.50, 0.53, and 0.26 for the CBS-QB3, CBS-APNO, and G3 methods respectively. By contrast, the mean values from the two atomization methods of −18.8 ± 1.1 and −18.6 ± 1.1 kcal mol^{-1} are significantly lower (*ca.* 0.9 kcal mol^{-1}), relative to the isodesmic reaction results.

We note that high level single-point CCSD(T)/aug-cc-pVnZ (n = D, T, Q) calculations by Gutowski and co-workers based on an optimized MP2/aug-cc-pVTZ geometry lead to $\Delta_f H^o_{298}(CH_3NO_2)$ = −16.5 kcal mol^{-1};[8] this included a small correction to the partition function of −0.2 kcal mol^{-1} to allow for hindered rotation. Energy refinements at single-point CCSD(T)/aug-cc-pV5Z and extrapolation to the complete basis set limit yielded a higher enthalpy of −16.3 kcal mol^{-1} compared to experimental data of −17.86[41] and −19.3 kcal mol^{-1}.[51b] Presumably, such a difference can be attributed to the MP2 geometry used in these single point calculations, while according to,[62] the B3LYP functional used also in CBS-QB3 method provides better geometry parameters for simple nitrocompounds than CCSD(T).

Nitroethane. The isodesmic reactions 5 and 6 were used for the enthalpy of formation of nitroethane:

$$CH_3CH_2CH_3 + CH_3NO_2 \leftrightarrow \mathbf{CH_3CH_2NO_2} + CH_3CH_3 \quad (5)$$

$$CH_3CH_2OH + CH_3NO_2 \leftrightarrow \mathbf{CH_3CH_2NO_2} + CH_3OH \quad (6)$$

These reactions were chosen as they conserve groups and use well-defined hydrocarbon and alcohol reference compounds along with the nitromethane (see Table 1). The averaged $\Delta_f H°$ for nitroethane of −25.06 ± 0.07 kcal mol^{-1} is in excellent agreement with the −24.81 kcal mol^{-1} recommended by an authoritative source.[51a] A value of −24.48 kcal mol^{-1} can be derived using the 34.4 kcal mol^{-1} mean value from NIST Webbook data for liquid-state $EtNO_2$ (34.4 ± 0.1, 34.32 ± 0.26, 33.48 ± 0.3 kcal mol^{-1}) and the ΔH(vaporization) = 9.94 kcal mol^{-1} from ref 51d.

Ethyl Nitrite (Ethyl Ester of Nitrous Acid). The isodesmic approach was used here in choosing work reactions 7 and 8:

$$CH_3CH_2CH_3 + CH_3ONO \leftrightarrow \mathbf{CH_3CH_2ONO\text{-}\mathit{cis}{-}\mathit{trans}} + CH_3CH_3 \quad (7)$$

$$CH_3CH_2OH + CH_3ONO \leftrightarrow \mathbf{CH_3CH_2ONO\text{-}\mathit{cis}{-}\mathit{trans}} + CH_3OH \quad (8)$$

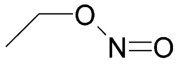
The two complete basis set (CBS−) and Gaussian type multilevel methods are fully consistent with each other showing excellent precision, as illustrated in Table 4. This supports the reaction analysis method and the enthalpy values recommended. The $\Delta_f H^o$(298 K) = −23.58 ± 0.12 kcal mol^{-1} (see Table 4) is 2.3 kcal mol^{-1} higher than the only available literature value of −25.9 kcal mol^{-1}.[30]

CH_3NO_2 *vs* CH_3ONO and $C_2H_5NO_2$ *vs* C_2H_5ONO. These theoretical methods consistently predict that RNO_2 is more stable than RONO, where R is an alkyl group. In the case of the methyl compound we compute a difference of 15.64 − (− 17.67) = 2.03 kcal mol^{-1}, in good agreement with the experimental result of 2.07 kcal mol^{-1} derived from recommended values by Cox and Pilcher in their comprehensive review.[41] Early studies in 1986 by McKee using MP2/6-31G(d) calculations[9] also showed CH_3NO_2 to be more stable than CH_3ONO, but by 5 or more kcal mol^{-1}.

The computations for the ethyl derivatives consistently show that the nitro isomer is more stable than the nitrite by some 1.48 kcal mol^{-1}. This is in contrast to the literature values, which suggest the nitrite is more stable by 1.5−2.4 kcal mol^{-1}.

We identify and report enthalpy values on the most stable isomers: *cis*-CH_3ONO, and *cis*−*trans*-C_2H_5ONO (Figure 1); that is the global minima on the conformation hypersurfaces are used for the evaluation of nitrite derivatives.

cis-trans EtONO



CH_3NO_2 *vs* $C_2H_5NO_2$. The difference in formation enthalpies between nitromethane and nitroethane is computed at 7.39 kcal mol^{-1}, which is close to the experimental data of 6.52 kcal mol^{-1} where both values come from the same group and experimental method.[55] Values recommended by Cox and Pilcher[41] are −17.86 and −24.38 kcal mol^{-1}, respectively, Table

TABLE 6: Heats of Formation at 298 K Computed by the Atomization Reaction (ARM) and Formation Reaction (FRM) methods (kcal mol^{-1})

species	method[a]	CBS-QB3	CBS-APNO	G3	mean	experiment
NO	ARM-1	20.76	22.04	21.80	21.53 ± 0.7	21.76 ± 0.02[39]
	ARM-2	20.89	22.17	21.93	21.66 ± 0.7	
	FRM	20.82	20.21	21.72	20.92 ± 0.8	
NO_2	ARM-1	6.02	6.39	8.13	6.85 ± 1.1	8.12 ±0.02[39]
	ARM-2	6.27	6.64	8.38	7.10 ± 1.1	
	FRM	6.53	5.98	6.35	6.29 ± 0.3	
HNO	ARM-1	24.61	26.11	26.41	25.71 ± 0.9	25.6 ± 0.6[46]
	ARM-2	24.73	26.24	26.53	25.83 ± 0.9	
	FRM	25.22	25.04	26.02	25.43 ± 0.5	
trans-HONO	ARM-1	−20.17	−18.73	−17.92	−18.94 ± 1.1	−18.87 ± 0.2[42]
	ARM-2	−19.92	−18.48	−17.67	−18.69 ± 1.1	
	FRM	−19.09	−19.85	−18.54	−19.16 ± 0.7	
cis-HONO	ARM-1	−19.81	−18.26	−17.35	−18.47 ± 1.2	−18.34 ± 0.2[43]
	ARM-2	−19.56	−18.01	−17.10	−18.22 ± 1.2	
	FRM	−18.74	−19.27	−18.06	−18.69 ± 0.6	
HNO_2	ARM-1	−12.30	−10.54	−9.98	−10.94 ± 1.2	−10.9 ± 0.1[30] [b]
	ARM-2	−12.05	−10.29	−9.73	−10.69 ± 1.2	
	FRM	−11.23	−11.91	−10.35	−11.16 ± 0.8	
$HONO_2$	ARM-1	−35.21	−32.99	−31.70	−33.30 ± 1.8	−32.1 ± 0.1[30]
	ARM-2	−34.84	−32.61	−31.32	−32.92 ± 1.8	
	FRM	−33.69	−34.18	−32.51	−33.46 ± 0.9	
cis-MeONO	ARM-1	−17.78	−16.92	−15.55	−16.75 ± 1.1	−15.64 ± 0.20[30]
	ARM-2	−17.58	−16.72	−15.35	−16.55 ± 1.1	
	FRM	−15.62	−16.30	−17.07	−16.33 ± 0.7	
$MeNO_2$	ARM-1	−19.89	−18.75	−17.68	−18.77 ± 1.1	−17.86 ± 0.15[41]
	ARM-2	−19.69	−18.55	−17.48	−18.57 ± 1.1	
	FRM	−17.73	−18.14	−19.20	−18.36 ± 0.8	
cis−*trans*-EtONO	ARM-1	−25.10	−24.72	−22.98	−24.27 ± 1.1	−25.9[25]
	ARM-2	−24.95	−24.57	−22.83	−24.12 ± .1	
	FRM	−21.87	−23.68	−24.09	−23.21 ± 1.2	
$EtNO_2$	ARM-1	−26.75	−26.55	−24.81	−26.04 ± 1.1	−24.38 ± 0.3[41]
	ARM-2	−26.60	−26.40	−24.66	−25.89 ± 1.1	
	FRM	−23.52	−25.52	−25.92	−24.99 ± 1.3	
NH_2CH_2COOH[c]	ARM-1	−94.32	−92.68	−93.93	−93.64 ± 0.8	−93.3 ± 1.1[47a]
glycine	ARM-2	−94.17	−92.53	−93.78	−93.49 ± 0.8	
	FRM	−91.08	−92.89	−93.79	−92.59 ± 1.4	
aci-NEt	ARM-1	−15.91	−14.82	−13.17	−14.63 ± 1.4	
	ARM-2	−15.76	−14.67	−12.92	−14.45 ± 1.4	
	FRM	−12.67	−13.79	−14.18	−13.55 ± 0.8	
aci-NMe	ARM-1	−6.14	−4.18	−3.25	−4.52 ± 1.5	
	ARM-2	−5.94	−3.98	−3.05	−4.50 ± 1.3	
	FRM	−3.98	−3.57	−4.77	−4.11 ± .6	

[a] For explanations of differences between ARM-1, ARM-2, and FRM methods, see the text and the Appendix. [b] Evaluated value. [c] Glycine is an isomer of nitroethane ($EtNO_2$) and presented here for comparison.

TABLE 7: Bond Dissociation Energies of Methyl Nitro Compounds (kcal mol^{-1})

species	$CH_3{-}NO_2$	*cis*-$CH_3{-}ONO$	*cis*-$CH_3O{-}NO$	$H{-}CH_2NO_2$
CBS-QB3	61.52	59.41	42.27	101.3
CBS-APNO	59.94	57.87	42.61	
G3	59.70	57.81	41.59	101.1
mean	60.39 ± 0.99	58.36 ± 0.91	42.16 ± 0.52	101.2 ± 0 14
experiment	60.59,[30] 59.4,[9] 60.1[32]	57.7[34]	41.70[30]	107.5[51]
MCSCF[a]	54.4[10]			
QCISD[b]	51.1[10]			
CCSD(T)[c]	58.3[6]		38.5[6,e]	
CCSD[d]	58.55[27]			
CCSD(T)[a]		59.24[13]	39.2[13]	102.5[13]
G2MP2[f]	61.9[24]			
MRCI	60 ± 2[71]			

[a] Basis set 6-311++G(2d,2p). [b] Basis set 6-311G(d,p). [c] Basis set CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311+G(3df,2p). [d] Basis set cc-pVDZ. [e] Basis set *trans*-CH_3ONO, while the *cis*-isomer is more stable. [f] G2MP2//B3LYP/6-311++G(2d,2p)

1. Methanol and ethanol might be reasonable comparison molecules where the respective enthalpies are −48 and −56 kcal mol^{-1}, a difference of 8 kcal mol^{-1}.

***aci*-Nitromethane $CH_2{=}N(O)OH$ (Methane Nitronic Acid).** The structure $CH_2{=}N(O)OH$ has the H−O−N−O fragment in a *cis* orientation as the stable form of methane nitronic acid (*aci*-nitromethane); see Figure 2.

The corresponding *trans* form appears to be a transition state on the potential energy surface with a 97 cm^{-1} imaginary frequency associated with rotation about the N−OH bond. This *trans* structure is less stable than the *cis* tautomer by 6.56 kcal mol^{-1}, which is the barrier height for rotation about the N−OH bond. The added stability of the *cis* form is because of O⋯H−O hydrogen bonding.

TABLE 8: Bond Dissociation Energies for Nitroethane and *cis−trans*-Ethyl Nitrite (kcal mol^{-1})

species	$C_2H_5{-}NO_2$	*cis−trans*-$C_2H_5{-}ONO$	*cis−trans*-$C_2H_5O{-}NO$
CBS-QB3	62.88	60.77	41.65
CBS-APNO	61.09	59.25	42.65
G3	61.88	60.05	41.93
mean	61.95 ± 0.89	60.02 ± 0.76	42.08 ± 0.52
experiment	60.8[2]		42.0 ± 1.3,[24] 2.32[52]
G2MP2			45.4[23]
CBS-Q	60.79[27]		44.5[23]
CCSD [a]	59.72[27]		

[a] cc-pVDZ basis set

TABLE 9: Bond Dissociation Energies for *aci*-Nitromethane (kcal mol^{-1})

species	$CH_2N(O){-}OH$	$CH_2N(OH){=}O$	$CH_2{=}N(O)OH$	$CH_2N(O)O{-}H$	$H{-}C(H)N(O)OH$
CBS-QB3	50.42	66.90	81.09	87.55	119.25
CBS-APNO	49.48	68.82	79.77	87.22	119.02
G3	49.26	67.85	78.40	86.70	118.81
mean	49.72 ± 0.62	67.85 ± 0.96	79.75 ± 1.35	87.15 ± 0.43	119.03 ± 0.22

The enthalpy of formation of methane nitronic acid at 298 K was evaluated using the isomerization work reaction to nitromethane:

$$\mathbf{CH_2}{=}N(O)OH \leftrightarrow CH_3NO_2 \tag{9}$$

in conjunction with our value for nitromethane, is − 3.45 ± 0.44 kcal mol^{-1} (Table 5) which is a mean value of −3.95, −3.27, and −3.13 kcal mol^{-1} at the CBS-QB3, G3, and CBS-APNO levels, respectively. The atomization procedure leads to − 4.52 ± 1.47 kcal mol^{-1}, (see Table 6, *vide infra*). Note that the heat of formation of *aci*-nitromethane at 0 K was evaluated in[16] as −1.17 kcal mol^{-1} using atomization procedure at the G1 level, which we convert to −4.38 kcal mol^{-1} at 298 K using a −3.21 kcal mol^{-1} temperature correction from CH_3NO_2.

The heat of formation of *aci*-nitroethane is −14.33 kcal mol^{-1}, using the work reaction 10 below, and −15.84 kcal mol^{-1} using the atomization energy procedure; both calculations are at the CBS-QB3 level:

$$CH_3{-}CH{=}N(O)OH + CH_2{=}CH_2 \leftrightarrow CH_2{=}N(O)OH + CH_3CH{=}CH_2 \tag{10}$$

aci-Nitromethane is predicted to be less stable than nitromethane by 14.25 ± 0.44 kcal mol^{-1} (mean of CBS-QB3, G3, and CBS-APNO calculations, 13.75, 14.43, and 14.57 kcal mol^{-1}, respectively). There is agreement with the results of G1[16] and G2MP2[24] calculations where the respective difference of 14.1 and 14.7 kcal mol^{-1} is reported; but we are not in agreement with Murrell et al.,[56] who reported a value of 21.9 kcal mol^{-1} using MP2/6-31G(d). Our result from the B3LYP/6-31G(d,p) level of theory is 14.71 kcal mol^{-1}, which supports the 14.25 kcal mol^{-1} value.

The small energy difference between the two *aci*-nitro and nitromethane tautomers, ~14.5 kcal mol^{-1}, suggests that C-substitution of nitromethane can lead to enhanced tautomerism. We find that this value is sensitive to substitution of the alkyl group. Calculations for $EtNO_2$ and $MeCH{=}N(O)OH$ at the CBS-QB3 level reduce the energy difference to 10.9 kcal mol^{-1} between the two isomers. This is consistent with the semiempirical MINDO calculations of Salim and Khalil[63] that show methyl substitution stabilizes the *aci*-form of nitromethane more than the nitro form.

Results from our composite method calculations demonstrate that nitro alkanes are more stable than corresponding nitrite isomers as expressed in Tables 3, 4, and 6. Methyl and ethyl nitrites are less stable than nitro forms by 2.1 and 1.7 kcal mol^{-1} respectively and they are more stable than corresponding *aci*-forms by 12.5 kcal mol^{-1} at the CBS-QB3 level.

Below we discuss the results of enthalpy calculations at 298 K using the alternative formation (FRM) and two atomization reaction (ARM-1 and ARM-2) methods for comparison.

III.2. $\Delta_f H^o_{298}$ *via* Formation Reaction Energies.

One relatively straightforward calculation scheme for heats of formation of a molecule is the formation reaction method (FRM) $\Delta H_f(298{+}o)$ schematically described in Table 2. The FRM method computes enthalpy of the formation of target molecules at 298 K from elements for which $\Delta_f H^o(298.15K)$ is assigned to be zero. For systems including condensed phase carbon atoms (see Table 6) we have added vaporization energies of C atoms equal to the formation enthalpies by opposite sign as recommended by in[53] (see also Table 1). The results on heats of formation we present in Table 6 are for comparison with the results of atomization scheme calculations discussed below. The FRM results often show higher differences (one or more kcal mol^{-1}) from the experimental data for $\Delta_f H^o_{298}$ and the values calculated by atomization and work reactions. The FRM differences also tend to increase for the larger molecules.

III.3. $\Delta_f H^o_{298}$ *via* Atomization Reaction Energies.

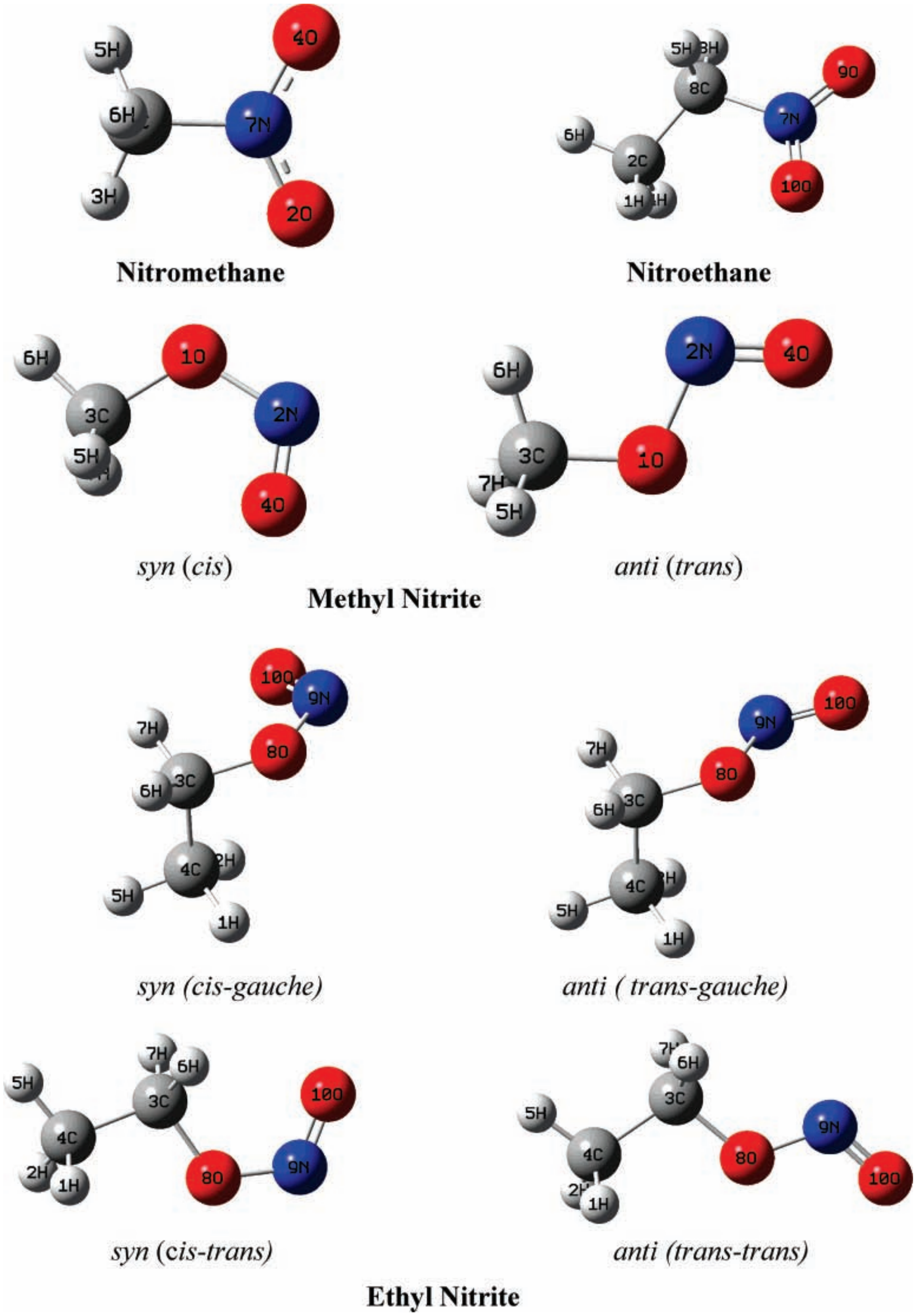
Atomization reactions are the most common method used by computational chemistry researchers to determine enthalpy of formation; here enthalpies are computed from the calculated ΔH_{rxn} and the experimental (known) enthalpies for constituent atoms.[29,50,53] In this study we utilize and describe two schemes to evaluate the heats of formation, $\Delta_f H^o_{298}$ with the atomization reaction methods (ARM-1 and ARM-2).

ARM-1 uses:

- Calculated values of $\Delta_f H$ of the atoms and molecule $\Delta_f H(M)$ at 0 K.
- Calculated $\Delta_f H_{rxn}$ at 0 K (atomization reaction).
- Experimental (literature) values of $\Delta_f H^o$ of the atoms at 0 K.
- Thermal corrections (298 K) for the atoms from experiment.
- Thermal corrections for the molecule from calculation.

ARM-2 uses:

- Calculated values of $\Delta_f H$ of the atoms and molecule $\Delta_f H(M)$ at 298 K.
- Calculated $\Delta_f H_{rxn}$ at 298 K (atomization reaction).
- Experimental (literature) values of $\Delta_f H^o$ of the atoms at 298 K.
- Thermal corrections (298K) for the atoms and molecule used in $\Delta_f H_{rxn}$ at 298 K from the Gaussian code.



Nitromethane **Nitroethane**

syn (*cis*) *anti* (*trans*)

Methyl Nitrite

syn (cis-gauche) *anti (trans-gauche)*

syn (*cis-trans*) *anti (trans-trans)*

Ethyl Nitrite

Figure 1. Nitroalkanes and alkyl nitrites.

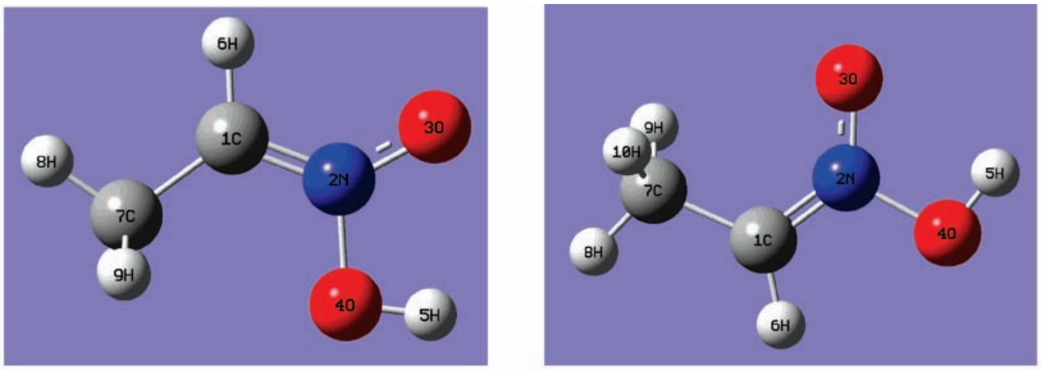
The ARM-1 and ARM-2 methods are described in Table 2 and example calculations are in the Appendix for each of employed methods.

Enthalpies of formation at 298 K, $\Delta_f H^o{}_{298}$, as evaluated by the two atomization schemes are reported in Table 6 for 14 molecules (the six target molecules of this study) plus eight additional $H_xN_yO_z$ species for added evaluation with literature.

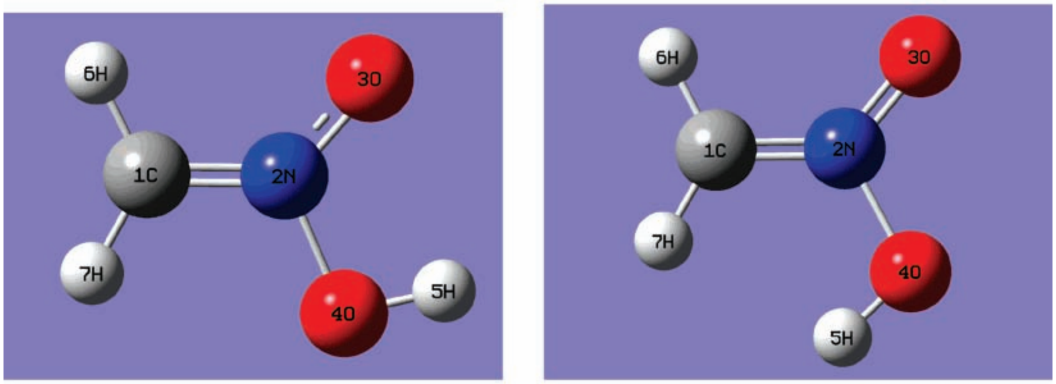
Data in Table 6 illustrate that enthalpy values from the ARM-1 method consistently result in slightly lower $\Delta_f H^o{}_{298}$ enthalpies (from 0.1 to 0.4 kcal mol^{-1}), relative to the ARM-2. The accuracy of the G3 calculated enthalpy values, from comparison to the evaluated enthalpies of the seven reference $H_xN_yO_z$molecules, is clearly best from the ARM-1 calculation method. The G3 method overestimates the recommended values when using the ARM-2 method and atom enthalpies, again in the 0.1−0.4 kcal mol^{-1} range.

The CBS-QB3 calculated values are more accurate when the ARM-2 atomization reaction method is utilized. In general, the CBS-QB3 values from atomization reactions result in lower enthalpies compared to CBS-APNO, G3, and experimental data.

CBS-APNO is our highest level theory based on QCISD/6-311G(d,p) final geometries and the enthalpy data are a *posteriori* more consistent for the seven smaller molecules. The mean deviation for the first seven $H_xN_yO_z$species is 0.19 kcal mol^{-1} for the ΔH_f(ARM-1), even with a 1.7 kcal mol^{-1} deviation for NO_2. A larger deviation of 1.9 kcal mol^{-1} occurs with the ΔH_f(ARM-2) values. Both atomization methods with CBS-APNO



(*Cis*-*cis*) *aci*-$C_2H_5NO_2$ (*Cis*-*trans*) *aci*-$C_2H_5NO_2$



aci-CH_3NO_2(*cis*) *aci*-CH_3NO_2(*trans*)

Figure 2. *Aci*-Form nitroalkanes at CBS-QB3 composite, *viz.*, B3LYP/6-311(2d,d,p) level.

result in enthalpies that are several tenths of a kcal mol^{-1} higher than the experimental values, with the major exception being NO_2.

Atomization Results for Target Methyl and Ethyl Nitrogen Oxides. The results for the four target methyl and ethyl nitro /nitrite molecules in this study are evaluated against the experimental data for nitromethane and methyl nitrite. The ΔH_f^o(298) data of -25.1 kcal mol^{-1} for nitroethane and -23.6 kcal mol^{-1} for *cis*-ethyl nitrite obtained in this study is evaluated for the corresponding ethyl moieties, (see work reaction data Table 4). The G3 method with ARM-1 values shows the closest overall agreement with a mean deviation of 0.24 kcal mol^{-1} for the four carbon NO_x species. The mean deviation with the ARM-1 parameters is 0.5 kcal mol^{-1} (overestimation). The CBS-QB3 again shows good agreement with the ARM-2 atom values with a mean variation of -0.42 and $+ 1.88$ kcal mol^{-1} for the NIST data set.

CBS-APNO calculations span the recommended values equally with a $+1.2$ and -1.1 kcal mol^{-1} mean deviation for the respective methods.

In general, we conclude that the results of three composite methods are close to each other. The small increase in $\Delta_f H^o_{298}$ from $\Delta_f H^o$(ARM-2) parameters of 0.2 kcal mol^{-1} over $\Delta_f H^o$(ARM-1) slightly enhances the discrepancies between theory and experiment.

Differences in $\Delta_f H^o_{298}$ from the ARM-1 and ARM-2 Methods. The first atomization reaction scheme (ARM-1) is based on calculated heats of formation at zero K with the inclusion of thermal enthalpy increments (this is a commonly used method; it is recommended in Gaussian tutorials and related publications[29,50]). The ARM-2 scheme is similar to the work reaction approach in this study, but uses atoms in place of molecules for products (see section III.1). ARM-2 uses computed heats of formation of the molecule, the constituent atoms (as reaction products), and the heat of reaction at 298 K.

Enthalpies of formation, $\Delta_f H^o_{298}$, evaluated by the two methods are presented in Table 6 for target molecules of this study plus an additional seven $H_xN_yO_z$ reference molecules. In principle, these two methods are identical and should lead to the same results by definition; however, in practice there is often a difference depending on the selected experimental or theoretical parameters for the thermal energies. We find the errors from the atomization analysis to be 0.2−0.4 kcal mol^{-1}, and additive. The errors will be higher for larger molecules. The main error in the ARM-2 results is judged to result from omission of contributions from low-lying electronic levels in the carbon and oxygen atoms (as well as S, B, F, Cl, Si, Al, etc.). The ARM-2 *method* uses theoretical values for atoms at 298 K from Gaussian outputs, which omits the electronic component of the integrated heat capacity. Gaussian assumes that the first electronic excitation energy is much greater than (thermal energy) k_BT and the first and higher excited states are inaccessible at any temperature (see e.g., ref 50b). As a result, the electronic heat capacity and the thermal energy due to electronic motion are both zero. Systematic corrections have to be added (by the researcher) to heats of formation of such atoms at 298 K. For example, $\Delta_f H^o$(298.15K) for oxygen and carbon atoms have to be corrected by $+0.126$ and -0.05 kcal mol^{-1}, when using data presented in Table 1 (see Appendix for details). Note that for the carbon atom we used an improved experimental value of $\Delta_f H^o_{298} = 170.11$ kcal mol^{-1}, recently reported by Ruscic and coworkers.[64] With these corrected atom energies, one can use Gaussian outputs at 298 K (directly) and the ARM-2 method *via* a conventional work reaction approach.

The results of atomization procedure strongly depend on the empirical parameters ($\Delta_f H^o$ atoms, ΔH_T) utilized and the accuracy of atomization energy calculation within the given scheme. Calculation errors are different in value depending on the method chosen and the systematic fluctuations can be corrected using more complicated scaling schemes. The composite quantum chemical methods include core/valence and atomic spin−orbit effects, in addition to corrections implicitly included *via* the “higher order correction”. However, they neglect scalar relativistic effects, which can be as large as 1−2 kcal mol^{-1} for larger and branched hydrocarbons with these NOx moieties.

III.4. Bond Dissociation Energies. The determination of bond dissociation energies[57] allows the identification of the weakest bonds in molecules and this enables the evaluation of initiation reactions that are important for kinetic modeling. Bond energies are reported from the calculated difference of the respective reaction enthalpy, where the enthalpies of parent molecule and product species are calculated in this study; the data correspond to the standard temperature of 298.15 K.

The mean value obtained for RC−NO$_2$ bond dissociation in nitromethane D(H$_3$C−NO$_2$) is 60.39 ± 0.99 kcal mol^{-1}. This is in excellent agreement with the experimental data (60.59, 59.4, and 60.1 kcal mol^{-1}, see Table 7) and the recommended by Luo[2] value of 60.8 based mainly on an earlier review[52a] and the more recent work by Miroshnichenko et al.[58] Several calculated values are also in reasonable agreement with our data: 58.3,[6] 61.9,[24] and 58.55 kcal mol^{-1}.[27] The RC−NO$_2$ bond in nitroethane is slightly stronger at 61.95 kcal mol^{-1} in moderate agreement with an experimentally based value of 60.8 kcal mol^{-1}, as listed in Table 8.

For D_0(MeO−NO), our computed value of 42.16 ± 0.52 kcal mol^{-1} is in satisfactory agreement with the 41.8 kcal mol^{-1} derived from pyrolysis experiments by Batt and Milne.[52c] The EtO−NO computed bond dissociation energy of 42.08 kcal mol^{-1} is almost the same as for the methyl species and is in excellent agreement with the only experimental value of 42.0 ± 1.3 kcal mol^{-1}; see Table 8.

Unfortunately there are no reliable experimental values available for D(R−ONO) although Beigersbergen et al. estimated it at 2.5 eV or 57.7 kcal mol^{-1} for R = Me while studying the fragmentation of neutralized radical cations of nitromethane isomers.[34] Hence, our computed value of 58.36 kcal mol^{-1} is probably the most reliable (Table 7). The corresponding ethyl compound is calculated to have a stronger C−O bond at 60.02 kcal mol^{-1}; see Table 8.

Literature values show a variance of 11 kcal mol^{-1} for the C−H bond in nitromethane. Knobel et al.[51b] reported 107.5 kcal mol^{-1}, which is considerably higher than the 97.4 kcal mol^{-1} of Bordwell and Satish[51c] derived from electrochemical measurements. Miroshnichenko et al. also report a low value of 96.3 kcal mol^{-1}.[58] Our calculated number of 101.2 kcal mol^{-1} bridges the above data, Table 7.

We have also determined theoretical values for dissociation energies of the molecular systems studied here to radicals C$_2$H$_5$O$^\bullet$ (X$^2\Sigma$) and $^\bullet$NO (X$^2\Pi$) in their doublet ground states. Experimental data range from 35 and 46.8 kcal mol^{-1} with the most recent value of 42.32 kcal mol^{-1},[52] our average value is 42.1.

Bond dissociation energies for the *aci*-tautomer of nitromethane are evaluated and presented in Table 9. One can see that OH-detachment requires only *ca.* 50 kcal mol^{-1} energy while other decomposition pathways are not energetically unfeasible.

IV. Conclusion

The computed enthalpies of formation *via* isodesmic work reactions and bond dissociation energies for nitromethane and methylnitrite are in satisfactory agreement with the limited experimental data available. Recommended values of $\Delta_f H^o{}_{298}$ for nitroethane and ethylnitrite follow the relative trend of the corresponding methyl system at −25.1 and −23.6 kcal mol^{-1}, respectively, where ethyl nitrite is by 2.3 kcal mol^{-1} higher than the lone experimental value.

In general, nitro alkanes are more stable than corresponding nitrite isomers. Methyl and ethyl nitrites are less stable than nitro forms by 2.1 and 1.7 kcal mol^{-1} respectively, and they are more stable than corresponding *aci*-forms by 12.5 kcal mol^{-1}. Enthalpy and bond energies for *aci*-nitromethane and *aci*-nitroethane are reported for the first time. The establishment of firm enthalpy values for the methyl− and ethyl−nitro compounds provides a basis for future work on the higher homologues.

Carbon−nitrogen and carbon−oxygen bonds in the nitroethane and ethylnitrite are *ca.* 2 kcal mol^{-1} stronger than in the corresponding methyl species and RO−NO bonds are similar in both systems at 42 kcal mol^{-1}.

A set of thermal corrections to atomic enthalpies at 0 K is developed and for use of a direct atomization calculation of enthalpies at 298.15 K using computation outputs at the same temperature for carbon, nitrogen, oxygen, and hydrogen containing molecules.

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Appendix

Atomization Analysis for Enthalpy of Formation at a Given Temperature, e.g., 298.15K (for simplicity we use 298 K ≈ 298.15 K in the equations below). The atomization procedure includes a hypothetical, balanced reaction for the target molecule, such as C$_2$H$_6$ = 2C + 6H or HNO = H + N + O, where all species are in the gas phase.

- The absolute enthalpy of the target molecule and each of the atoms is computed at 0 K.
- This data is used to calculate the enthalpy of reaction $\Delta H_{\rm rxn}$(0 K), which is the theoretical (calculated) value of the atomization enthalpy of a reactant molecule at given temperature (0K here):

$$\Delta H_{\rm rxn}(0\ {\rm K}) = \Sigma H_{\rm product\ atoms}(0\ {\rm K}) - H_{\rm reactant\ molecule}(0\ {\rm K}) \qquad ({\rm I})$$

- To find the enthalpy of formation of the target molecule, ΔH_f(M, 0K), one uses the calculated $\Delta H_{\rm rxn}$(0 K) and the known (from experiment or evaluated theoretically) ΔH_f(A, 0K) values of each atom at 0 K in eq I above.
- To convert this ΔH_f (M, 0K) into a ΔH_f (M, TK) at some temperature, typically 298.15 K, one adds the temperature corrections T_c to each of the products and reactants resulting in

$$\Delta H_{\rm rxn}(298{\rm K}) = \left(\Sigma H_{f,\rm prods}(0{\rm K}) + \Sigma T_{c,\rm prods}\right) - \left(\Sigma H_{f,\rm reacts}(0{\rm K}) + \Sigma T_{c,\rm reacts}\right)$$

where T_c is the thermal correction from 0 to 298.15 K.

The T_c values are determined from statistical mechanics,[50b] and the properties of molecule(s) and atom(s), which are derived from the calculations.

Temperature dependence of enthalpy includes the integrated heat capacity term

$$\Delta_f H_T = \Delta_f H_0 + \int_0^T C_p(T)\,\mathrm{d}T \qquad \text{(II)}$$

which is the enthalpy increment: $\Delta H_T(M) - \sum \Delta H_T(\text{elements})$.

It is common to take $\Delta H_T(A)$ corrections for atoms from experiment, $T_{c,\text{expt}}(\text{A})$, while $\Delta H_T(M)$ is computed.

Contributions to $\Delta H_T(M)$ come from translation, rotation, vibration, and electronic motions. For general case of nonlinear polyatomic molecules, translational (E_t) and rotational (E_r) terms are equal to $^3/_2RT$ at the $E_\text{e} = 0$ (*vide infra*), while contribution from molecular vibration is

$$E_\text{v} = R\Sigma\Theta_{\upsilon,i}\{^1/_2 + 1/(e(\Theta_{\upsilon,i}/T - 1) - 1)\}$$

where $\Theta_{\upsilon,i} = h\nu_i/k_\text{B}$ is a characteristic vibrational temperature ($\Theta_{\upsilon,i}/2$ is the zero point vibrational energy) from each i vibrational mode. In the example analysis below, results from the Gaussian code are used with low-frequency modes included in the computations. Some of the low-frequency modes may be torsions for internal rotation. These internal rotors can be treated separately, for more accuracy by Gaussian or special computer codes such as Rotator or VIB.[65]

Traditional Atomization Reaction Method for Enthalpy of Formation (ARM-1) or $\Delta H_f(o+tc)$. The atomization approach identified here as ARM-1 and recommended in Gaussian tutorials and related publications[29,50,53] is as follows:

•The atomization energies, $\sum D_0(0\text{K})$are computed for all atoms "A" and respective molecules "M" using calculated electronic energies and zero-point energy corrections (theoretical values at 0 K):

$$\Sigma D_\text{o}(\text{M}) = \Sigma E_0(\text{Theor, A}) - E_0(\text{Theor, M}) \qquad \text{(A1)}$$

•Enthalpies of formation for molecules, $\Delta_f H^\text{o}(\text{M, 0 K})$ are then computed using experimental (known) enthalpies of formation for atoms at 0 K (see Table 2 and discussion below) and the atomization reaction energy from eq A1.

$$\Delta_f H^\text{o}(\text{M, 0 K}) = \Sigma\Delta_f H^\text{o}(\text{A, 0 K}) - \Sigma D_\text{o}(\text{M, 0 K}) \qquad \text{(A2)}$$

Formation enthalpies at 298 K are computed as

$$\Delta_f H^\text{o}(\text{M, 298K}) = \Delta_f H^\text{o}(\text{M, 0 K}) + T_{c,\text{calc}}(\text{M}) - \Sigma T_{c,\text{expt}}(\text{A}) \qquad \text{(A3)}$$

where $T_{c,\text{calc}}(\text{M}) = H^\text{o}(\text{M, 298 K}) - H^\text{o}(\text{M, 0 K})$ is a theoretical value of the temperature correction parameter (thermal energy content) for a molecule. The $T_{c,\text{expt}}(\text{A}) = H^\text{o}(\text{A, 298 K}) - H^\text{o}(\text{A, 0 K})$ values are the experimental values for the constituent atoms in their reference states. A set of recommended temperature corrections for atoms is listed in Table 1 (second set). One can see that they are derived from corresponding values for elements in their standard states. For atoms of interest they have correspondingly modified from gaseous elements: H_2 (2.024), N_2 (2.072), O_2 (2.075).[47] For C atoms represented by graphite with a solid reference state, it is equal to 0.25 kcal mol^{-1}.

This $\Delta H_f(o+tc)$ method is outlined by Curtis et al.[29, 50a] and it is commonly used (Table 2). The method computes the 0 K atomization enthalpy, converts it to the enthalpy of formation at 0 K, $\Delta_f H^\text{o}(\text{A, 0 K})$, and then the 0 K enthalpy of formation of the target molecule converts to 298 K.

Simplified Atomization Reaction Method for Enthalpy of Formation (ARM-2) or $\Delta H_f(298+tc')$. In this study, we also utilize an alternate atomization method: $\Delta H_f(298+tc')$, which is a direct atomization calculation method ARM-2 using computed absolute enthalpy values for molecules and for atoms at 298 K. This is a more convenient approach as shown in eq A4.

$$\Delta_f H^\text{o}(\text{M, 298 K}) = \Sigma\Delta_f H^\text{o}(\text{A, 298K}) - \Sigma\, D_\text{o}(\text{M, 298K}) \qquad \text{(A4)}$$

Atomization energies (eq A1) are computed using enthalpy of reaction at 298 K (in place of E_0) and experimental heats of formation of constituent atoms at the same temperature, 298 K.

The ARM-2 scheme $\Delta H_f(298+\text{tc}')$ computes atomization enthalpy at 0 K and then converts it to 298 K using $T_c(\text{M}) = H_{298}(\text{M}) - H_0(\text{M})$ of the target molecule and $T_c'(\text{A}) = H_{298}(\text{A}) - H_0(\text{A})$ for the isolated atoms (upper set of parameters in Table 1). This 298 K atomization enthalpy is then used to determine enthalpy of formation $\Delta_f H^\text{o}(\text{M, 298 K})$ by using the enthalpies of formation of the atoms at 298 K $\Delta_f H^\text{o}(\text{A, 298 K})$.

The results of two approaches should be the same by definition but they can differ depending on the theoretical values for the atom temperature corrections and/or the experimental values for these parameters employed (Table 2). The ARM-1 method relies upon enthalpies of atoms at 0 K $\Delta_f H^\text{o}(\text{A, 0 K})$ derived from elements and corresponding temperature corrections. ARM-2 uses experimental values of the heats of formation of atoms at 298 K, $\Delta_f H^\text{o}(\text{A, 298 K})$, usually from NIST or CODATA or other evaluation, and the calculated enthalpies of molecules and atoms at the same temperature.

Examples of the Two Calculation Methods. The 0 K enthalpies (ARM-1), and enthalpies at 298 K (ARM-1, ARM-2) are determined using atomization energy of HNO molecule calculated at the CBS-QB3 composite level of theory, in order to illustrate the difference between the two approaches. The example calculation also permits some analysis on the importance and value of the temperature corrections in the estimation schemes,

Scheme ARM-1 or $\Delta H_f(o+tc)$.

$$\begin{aligned}\Delta_f H^\text{o}(\mathbf{HNO}, 0\text{ K}) &= \Delta_f H^\text{o}(\mathbf{H}, 0\text{ K}) + \Delta_f H^\text{o}(\mathbf{N}, 0\text{ K}) + \\ &\qquad \Delta_f H^\text{o}(\mathbf{O}, 0\text{ K}) - \Sigma D_\text{o}(\mathbf{HNO}, 0\text{ K}) \\ &= 51.6336 + 112.534 + 58.987 - \\ &\qquad \Sigma D_\text{o}(\mathbf{HNO}, 0\text{ K}) \\ &= -223.197 - \Sigma D_\text{o}(\mathbf{HNO}, 0\text{ K})\text{ kcal mol}^{-1}\end{aligned}$$

where $\sum D_0(\mathbf{HNO}, 0\text{ K})$ is a theoretical value of atomization energy at 0 K, (heat of atomization reaction calculated at 0 K).

$$\Delta_f H^\text{o}(\mathbf{HNO}, 0\text{ K}) = 223.157 - 197.84 = 25.317\text{ kcal mol}^{-1}$$

To determine the heat of formation of HNO at 298 K, one adds the corresponding temperature corrections for molecule and subtracts the corrections for atoms:

$$\begin{aligned}\Delta_f H^\text{o}(\mathbf{HNO}, 298\text{ K}) &= \Delta_f H^\text{o}(\mathbf{HNO}, 0\text{ K}) + T_{c,\text{calc}}(\mathbf{HNO}) - \\ &\qquad T_c(\mathbf{H}) - T_c(\mathbf{N}) - T_c(\mathbf{O}) \qquad (5) \\ &= \Delta_f H^\text{o}(\text{HNO, 0 K}) + T_{c,\text{calc}}(\text{HNO}) - \\ &\qquad \Sigma T_c'(\text{X})\end{aligned}$$

where the sum is over all atoms.

$$T_{c,\mathrm{calc}}(\mathbf{HNO}) = 627.5095\,\{\Delta H_{\mathrm{calc}}(\mathbf{HNO}, 298\ \mathrm{K}) - \Delta H_{\mathrm{calc}}(\mathbf{HNO}, 0\ \mathrm{K})\} = 627.5095\,(-130.319502 + 130.323285) = 2.384\ \mathrm{kcal\ mol^{-1}}.$$

This sum is the calculated T_c(M) value for molecule.

T_c(H), T_c(N), and T_c(O) are derived from corresponding elements in their standard states (*vide infra*) experimental corrections for atoms H, N and O, respectively, Table 1.

The resulting $\Delta_f H^o(\mathbf{HNO}, 298\ \mathrm{K}) = 25.317 + 2.384 - (1.01 + 1.04 + 1.04) = 25.32 - 0.703 = 24.61$ kcal mol^{-1} cf. experimental[46] 25.6 kcal mol^{-1}.

Scheme ARM-2 or $\Delta H_f(298+tc')$. At 298 K, the following holds:

$$\Delta_f H^o(\mathbf{HNO}) = \Delta_f H^o(\mathbf{H}) + \Delta_f H^o(\mathbf{N}) + \Delta_f H^o(\mathbf{O}) - \Sigma D_o(\mathbf{HNO}) \quad (6)$$

where:

$$\Sigma D_o(\mathbf{HNO}) = 627.5095\{\Delta H_{\mathrm{calc}}(\mathbf{H}) + \Delta H_{\mathrm{calc}}(\mathbf{N}) + \Delta H_{\mathrm{calc}}(\mathbf{O}) - \Delta H_{\mathrm{calc}}(\mathbf{HNO})\}$$

At 298 K, the calculation for the HNO molecule leads to the following results:

$$\Delta_f H^o(\mathbf{HNO}, 298\ \mathrm{K}) = (52.103 + 112.97 + 59.555) - 627.5\,(-0.497457 - 54.518183 - 74.985278 + 130.319502) = 224.628 - 199.91 = 24.72\ \mathrm{kcal\ mol^{-1}}$$

Comparison of the Two Methods. To compare the two methods and the T_c parameters, one can reassemble the values for the molecule and atoms that are in right-hand side of the last equation into a sum of 0 K data and corresponding temperature corrections to 298 K. Keep in mind that the corrections in the two methods can differ in value.

$$\Delta_f H^o(\mathbf{HNO}, 298\ \mathrm{K}) = \Delta_f H^o(\mathbf{H}, 0\ \mathrm{K}) + \Delta_f H^o(\mathbf{N}, 0\ \mathrm{K}) + \Delta_f H^o(\mathbf{O}, 0\ \mathrm{K}) - 627.5\{\Delta H_{\mathrm{calc}}(\mathbf{H}, 0\ \mathrm{K}) + \Delta H_{\mathrm{calc}}(\mathbf{N}, 0\ \mathrm{K}) + \Delta H_{\mathrm{calc}}(\mathbf{O}, 0\ \mathrm{K}) - \Delta H_{\mathrm{calc}}(\mathbf{HNO}, 0\ \mathrm{K})\} + T_{c,\mathrm{calc}}(\mathbf{HNO}) + T_c'(\mathbf{H}) - T_{c,\mathrm{calc}}(\mathbf{H}) + T_c'(\mathbf{N}) - T_{c,\mathrm{calc}}(\mathbf{N}) + T_c'(\mathbf{O}) - T_{c,\mathrm{calc}}(\mathbf{O})$$

Finally:

$$\Delta_f H^o(\mathbf{HNO}, 298\ \mathrm{K}) = \Delta_f H^o(\mathbf{HNO}, 0\ \mathrm{K}) + T_{c,\mathrm{calc}}(\mathbf{HNO}) - \Sigma\{T_{c,\mathrm{calc}}(\mathbf{A}) - T_c'(\mathbf{A})\} \quad (7)$$

where the sum is over all atoms.

Comparing data in eq 7 to data in eq 5, one can derive interrelation between temperature corrections in two approaches. We note here that $T_c(\mathbf{A})$ corresponds to $T_{c,\mathrm{calc}}(\mathbf{A}) - T_c'(\mathbf{A})$.

The calculated values of $T_{c,\mathrm{calc}}(\mathbf{H}) = T_{c,\mathrm{calc}}(\mathbf{N}) = T_{c,\mathrm{calc}}(\mathbf{O})$ obtained from the Gaussian output (*vide infra*) are $^3/_2RT + RT = 1.4811$ kcal mol^{-1} at 298.15 K which is the translational motion component of the + PV term in the theoretical values for atomic temperature corrections, ($^5/_2RT$). The comparative temperature corrections using the NIST webbook data (Table 1) for these atoms, can be characterized as: $T_c(\mathbf{H}) = 1.01$ kcal mol^{-1} when using atom-in- element data (Table 1, set no. 2) and $T_{c,\mathrm{calc}}(\mathbf{H}) - T_c'(\mathbf{H}) = 1.4811 - 52.103 + 51.6336 = 1.4811 - 0.4695 = 1.0116$ using the theoretical value along with the calculated difference between experimental data of $\Delta_f H^o$(298 K) and $\Delta_f H^o$(0 K) for respective atoms.

Data for the other atoms:

$$T_c(\mathbf{N}) = 1.04 \quad \text{and} \quad T_{c,\mathrm{calc}}(\mathbf{N}) - T_c'(\mathbf{N}) = 1.4811 - 112.97 + 112.53 = 1.48 - 0.44 = 1.04$$

$$T_c(\mathbf{O}) = 1.04 \quad \text{and} \quad T_{c,\mathrm{calc}}(\mathbf{O}) - T_c'(\mathbf{O}) = 1.4811 - 59.555 + 58.99 = 1.4811 - 0.565 = 0.917\ \mathrm{kcal\ mol^{-1}}$$

$$T_c(\mathbf{C}) = 0.25 \quad \text{and} \quad T_{c,\mathrm{calc}}(\mathbf{C}) - T_c'(\mathbf{C}) = 1.48 - 171.29 + 169.98 = 1.48 - 1.31 = 0.17\ \mathrm{kcal\ mol^{-1}}.$$

where the data for carbon atom $T_c(\mathbf{C}) = 0.25$ kcal mol^{-1}, and using the CODATA value for ΔH_f^o (C, 0K) of 169.98 kcal mol^{-1} [60] for 0 K and $\Delta H_f^o(\mathbf{C}, 298\mathrm{K}) = 171.29$ kcal mol^{-1}for atomic enthalpy of carbon atom at 298 K, one can obtain the enthalpy correction parameter as $T_{c,\mathrm{calc}}(\mathbf{C}) - T_c'(\mathbf{C}) = 1.48 - 171.29 + 169.98 = 1.48 - 1.31 = 0.17$ kcal mol^{-1}.

We note that use of the updated value for $\Delta H_f^o(\mathrm{C}, 0\mathrm{K}) = 170.11$ from Ruscic and co-workers[65] in the CODATA evaluation for the atomic enthalpy of carbon atom at 298.15 K, results in a new correction parameter: $T_{c,\mathrm{calc}}(\mathbf{C}) - T_c'(\mathbf{C}) = 1.48 - 171.29 + 170.11 = 1.4811 - 1.18 = 0.30$ kcal mol^{-1}. One can see the close agreement between two first atoms and substantial difference for the oxygen and carbon atoms.

The ARM-2 or the direct method $\Delta H_f(298+tc')$ can be used in the same manner as that for isodesmic and other work reactions, but this method requires a proper (revised) temperature correction data for the atoms. Examination of the Gaussian output data shows that the electronic part of integrated heat capacity is not included in Gaussian output for thermochemical energies. The $H_{298} - H_0$ energy includes translation, rotation, vibration, electronic, and nuclear contributions. Rotation and vibration contributions equal zero for atoms and nuclear is often negligible. Our values are listed in Table 1.

The ARM-2 takes the theoretical values from Gaussian output for atoms; but the electronic part of integrated heat capacity is not included. Gaussian assumes that the first electronic excitation energy is much greater than k_BT and the next and higher excited states are inaccessible at any temperature.[50b] This is done to simplify the electronic partition function and include only the electronic spin multiplicity of the molecule. The electronic heat capacity and the thermal energy due to electronic motion are both set to zero. Systematic corrections need to be added to the heats of formation of the atoms with these contributions at 298 K.

In order to obtain near identical results for both the ARM-1 and ARM-2 methods some additional corrections of Δ_i have to be employed:

- Oxygen atoms $\Delta_i(\mathbf{O}) = 0.565 - 0.44 = 0.125$ kcal mol^{-1} and new $\Delta_f H^o(\mathbf{O}, 298\ \mathrm{K}) = 59.43$ kcal mol^{-1} $= 59.555 - 0.125$.
- Carbon atoms $\Delta_i(\mathbf{C}) = 0.25 - 0.30 = -0.05$ kcal mol^{-1} and $\Delta H_f^o(\mathrm{C}, 298\mathrm{K}) = 171.29 + 0.05 = 171.34$ kcal mol^{-1}.

Use of these corrections allows a direct calculation for HNO that leads to the same 24.61 kcal mol^{-1} formation enthalpy as was evaluated *via* traditional method ARM-1 or $\Delta H_f(o+tc)$ method.

ARM-2 for Larger or More Complex Molecular Systems. The atomization technique is a powerful method when atomization energies are determined correctly (*vide* Discussion) and the calculated energy and atom energies are both accurate (include no systematic errors). Systematic errors do exist, however, and for large molecules, these errors accumulate and atomization reaction energies do not result in good enthalpy values. One corrective measure here is to calibrate (adjust) the atomization energies for larger molecules with temperature corrections using established data on molecules having similar formulations to the target species. One can use the relationships between temperature corrections in the two approaches and fit their difference to the best available (accurate) data for selected reference molecules in order to obtain a set of atom parameters, *viz.*, “*effective atoms values*”. These would substitute for the literature “isolated atom” parameters in the application. Carl Melius did something similar to this in his highly regarded bond additivity correction (BAC) method in the late 1980−1990s.[35] These semiempirical atom parameters can implicitly include the higher order corrections *via* parametrization (fitting) to the best data for molecules. Such a set of semiempirical parameters or “effective atomic enthalpies at 298 K” (EAE) can be used in routine large-scale molecular calculations for a class of molecules the atom parameter fit is relevant to. These fit values obviously are not the classical (exact) atomic enthalpies at 298 K, but a kind of “effective enthalpy equivalents”. These “equivalents” can then include contributions not considered in the determination of the accurate “atomic enthalpies”, which is a result of the fitting to accurate molecule data. Further improvement of this set of parameters can be achieved by extending the set of experimental reference molecules and result in further improvements in the parametrization of atomization procedure. This will be subject to the further study (see further discussion in ref 65).

We note that this approach is different from that proposed by Ibrahim and Schleyer[66] where atomic equivalents of the enthalpy of formation are computed by subtracting a parameter (the atom equivalents) for each atom in the molecule from its energy computed theoretically at the HF/6-31G(d) level. New atom equivalents are introduced also in ref 67, using molecular mechanics BP/DN**//MMFF energies to develop cost-effective approaches to formation enthalpies.

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