The heat of formation of NCO

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The heat of formation of NCO has been determined rigorously by state-of-the-art *ab initio* electronic structure methods, including Møller–Plesset perturbation theory from second through fifth order (MP2–MP5) and coupled-cluster and Brueckner methods incorporating various degrees of excitation [CCSD, CCSD(T), BD, BD(T), and BD(TQ)]. Five independent reactions were investigated to establish a consistent value for $\Delta H^\circ_{f,0}$(NCO): (a) $\mathrm{HNCO}(\tilde{X}\,^1A')\rightarrow \mathrm{H}(^2S)+\mathrm{NCO}(^2\Pi)$, (b) $\mathrm{HNCO}(\tilde{X}\,^1A')\rightarrow \mathrm{H}^+ +\mathrm{NCO}^-$, (c) $\mathrm{N}(^4S)+\mathrm{CO}\rightarrow \mathrm{NCO}(^2\Pi)$, (d) $\mathrm{HCN}+\mathrm{O}(^3P)\rightarrow \mathrm{H}(^2S)+\mathrm{NCO}(^2\Pi)$, and (e) $\mathrm{NH}(^3\Sigma^-)+\mathrm{CO}\rightarrow \mathrm{H}(^2S)+\mathrm{NCO}(^2\Pi)$. The one-particle basis sets employed in the study were comprised of as many as 377 contracted Gaussian functions and ranged in quality from [4*s*2*p*1*d*] to [14*s*9*p*6*d*4*f*] on the (C,N,O) atoms and from [2*s*1*p*] to [8*s*6*p*4*d*] on hydrogen. After the addition of bond additivity corrections evaluated from related reactions of precisely known thermochemistry, all five approaches were found to converge on the value $\Delta H^\circ_{f,0}(\mathrm{NCO})=31.4(5)$ kcal mol^{-1}. Appurtenant refinements were obtained for the heat of formation of isocyanic acid, $\Delta H^\circ_{f,0}(\mathrm{HNCO})=-27.5(5)$ kcal mol^{-1}, and hydrogen cyanide, $\Delta H^\circ_{f,0}(\mathrm{HCN})=31.9(5)$ kcal mol^{-1}. The final proposals for $\Delta H^\circ_{f,0}$(NCO) and $\Delta H^\circ_{f,0}$(HNCO) resolve outstanding discrepancies with experiment and provide updates for thermochemical cycles of relevance to combustion chemistry.

INTRODUCTION

The cyanato radical (NCO) is a key intermediate in the combustion of nitrogenous fuels in the atmosphere, a process in which NO_x pollutants are generated along with product molecular nitrogen.[1–4] Representative bimolecular pathways[1,2] for the formation of NCO radicals are the reactions

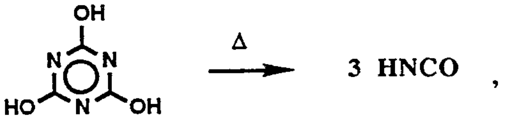
$$\mathrm{CN+O_2\rightarrow NCO+O}, \qquad (1)$$

$$\mathrm{CN+OH\rightarrow NCO+H}, \qquad (2)$$

and

$$\mathrm{HCN+O\rightarrow NCO+H}, \qquad (3)$$

whose relative importance depends on the specific flame conditions. Several schemes designed to reduce NO_x byproducts appearing in general combustion effluents also involve coupled elementary reactions wherein NCO assumes a prominent role. A notable example is the RAPRENO$_x$ process,[5] in which cyanuric acid [$(\mathrm{HOCN})_3$] is injected into combustion effluents and the ensuing elementary reactions include[6]



(4)

$$\mathrm{HNCO+OH\rightarrow NCO+H_2O}, \qquad (5)$$

$$\mathrm{NCO+NO\rightarrow N_2O+CO}, \qquad (6)$$

$$\mathrm{N_2O+M\rightarrow N_2+O+M}, \qquad (7)$$

and

$$\mathrm{N_2O+OH\rightarrow N_2+HO_2}. \qquad (8)$$

Above 1400 K the pair of reactions

$$\mathrm{NCO+(O,O_2)\rightarrow NO+(CO,CO_2)} \qquad (9)$$

becomes effective, contributing to a temperature boundary for NO_x reduction.[6]

Pioneering spectroscopic work on the $\tilde{X}\,^2\Pi\rightarrow\tilde{A}\,^2\Sigma^+$ band system of NCO was performed by Dixon in 1960[7] and followed by several optical absorption[8,9] and fluorescence studies[3,10–15] of this electronic transition. A variety of techniques has been applied directly to the ground electronic state, including gas-phase microwave,[16–19] electron paramagnetic resonance,[20,21] and far infrared laser magnetic resonance spectroscopy,[22–24] as well as matrix-isolation infrared methods.[8] The spectroscopic studies have provided a $^2\Pi_{1/2}$–$^2\Pi_{3/2}$ spin–orbit splitting parameter of 95.6 cm^{-1} for the $\tilde{X}\,^2\Pi$ state and an adiabatic excitation energy of 22 754 cm^{-1} for the $\tilde{A}\,^2\Sigma^+$ state.[7] In addition, a manifold of Renner–Teller vibronic band origins between 400 and 650 cm^{-1} has been observed upon excitation of the bending mode in the ground electronic state: $^2\Sigma^+$(441 cm^{-1}), $^2\Delta_{5/2}$(534 cm^{-1}), $^2\Delta_{3/2}$(628 cm^{-1}), and $^2\Sigma^-$(637 cm^{-1}).[7] Such complexities have made the NCO molecule of particular spectroscopic interest.

The heat of formation of the cyanato radical has proved to be an elusive quantity to establish. In 1970 Okabe[25] determined a photodissociation threshold of 178.3 ±0.2 kcal mol^{-1} for production of $\mathrm{H}(^2S)+\mathrm{NCO}(^2\Sigma^+)$ from HNCO, which yields $D_0(\mathrm{H{-}NCO})=113.0\pm0.2$ kcal mol^{-1} for dissociation to ground state fragments. From the contemporaneous value for the heat of formation of isocyanic acid, $\Delta H^\circ_f(\mathrm{NCO})=37.8\pm3.5$ kcal mol^{-1} was

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deduced. A similar value for ΔH_f°(38 ± 2.5 kcal mol^{-1}) is recommended in the JANAF thermochemical tables,[26] as derived from the same photodissociation threshold. In 1983 Sullivan and co-workers[27] observed an order of magnitude reduction in the fluorescence lifetime of the (100) vibrational level of $\tilde{B}\,^2\Pi$ NCO relative to the corresponding (000) state, which was interpreted in terms of an intervening, spin-allowed $N(^2D)+CO$ threshold and a concomitant upper bound $\Delta H_f^\circ(NCO) \geqslant 48$ kcal mol^{-1}. In 1986 Spiglanin *et al.*[28] performed photodissociation studies of HNCO in which nascent singlet imidogen fragments were detected by laser induced fluorescence, giving an onset energy of 118.7 kcal mol^{-1} for the production of $NH(\tilde{a}\,^1\Delta)+CO$. The resulting thermochemical revisions, $\Delta H_f^\circ(HNCO) = -24.9^{+0.7}_{-2.8}$ and $\Delta H_f^\circ(NCO) = +36.1^{+0.7}_{-2.8}$ kcal mol^{-1}, vitiated the interpretation of the previous fluorescence lifetime experiments on $\tilde{B}\,^2\Pi$ NCO. Supporting evidence for a lower value of $\Delta H_f^\circ(NCO)$ is also provided by Reaction (1), which proceeds with no appreciable barrier[29] and yields cyanato radicals with considerable bending excitation,[30,31] requiring the heat of formation of NCO to be substantially less than 44 kcal mol^{-1}.

Recently Setser and co-workers[32,33] have investigated the reactions

$$F+HNCO \rightarrow HF+NCO(^2\Pi) \quad (10)$$

and

$$F+NCO(^2\Pi) \rightarrow NF(\tilde{X}\,^3\Sigma^-)+CO \quad (11)$$

as sources of NCO and NF radicals in flow reactors at ambient temperatures. Uncertainty in the heat of formation of the cyanato radical has limited the interpretation of these experiments and hampered the determination of bounds on $\Delta H_f^\circ(NF)$. In 1989 Liu and Coombe[34] employed Reaction (10) to generate NCO radicals in a continuous discharge-flow apparatus and performed photolysis studies at 193 nm of the reaction

$$NCO(^2\Pi) \rightarrow CN(\tilde{X}\,^2\Sigma^+)+O(^3P). \quad (12)$$

A spectral simulation was used to extract vibrational and rotational population distributions in the CN fragments and to establish an upper limit on the internal excitation of the cyano radicals. The data require a *lower* limit, $\Delta H_f^\circ(NCO) > 37$ kcal mol^{-1}, unless the reactant internal energy distribution is significant.

In a very recent, high-level *ab initio* characterization of the $\tilde{X}\,^1A'$ state of isocyanic acid performed in our laboratory,[35] the recommended value of $\Delta H_{f,0}^\circ(HNCO)$ was lowered to -26.1 kcal mol^{-1}, and the direct theoretical data for the N–H bond energy were found to be consistent with $D_0(H\text{–}NCO) = 112 \pm 2$ kcal mol^{-1}. Because the range of theoretical predictions readily encompassed the more precise experimental N–H bond energy of Okabe,[25] its acceptance was recommended, which yielded the lowest $\Delta H_{f,0}^\circ(NCO)$ value yet proposed, 35.3 kcal mol^{-1}. While the article detailing these studies was in press, Cyr and co-workers[36] reported a fast beam study of NCO free radical photodissociation which further elevated the controversy on the heat of formation of this species. In particular, time-of-flight spectroscopy of the photodissociation products revealed that the spin-allowed $N(^2D)+CO$ channel becomes energetically accessible 20.3 kcal mol^{-1} above the origin of the $\tilde{B}\,^2\Pi$ state of NCO, an observation consistent with $\Delta H_{f,0}^\circ(NCO) = 30.5 \pm 1$ kcal mol^{-1}, a value significantly below all previous results. In order to definitively resolve this issue, the thermochemistry of the NCO radical has been reinvestigated here at the highest levels of *ab initio* theory which are currently feasible for this molecular system.

THEORETICAL METHODS

A precise value for the heat of formation of isocyanic acid provides a key reference point for the determination of $\Delta H_{f,0}^\circ(NCO)$, and thus the enthalpy change of isoelectronic Reaction (13) was revisited to refine our previous value[35] of $\Delta H_{f,0}^\circ(HNCO)$

$$\Delta H_{f,0}^\circ(HNCO):\quad CO_2+NH_3 \rightarrow HNCO+H_2O. \quad (13)$$

For similar reasons the heat of formation of HCN was investigated by means of Reaction (14).

$$\Delta H_{f,0}^\circ(HCN):\quad CO+NH_3 \rightarrow HCN+H_2O. \quad (14)$$

Thereafter, theoretical predictions for five independent reaction energies $[\Delta H_0^\circ(15)\text{–}\Delta H_0^\circ(19)]$ were used to establish the heat of formation of NCO, the corresponding evaluations of $\Delta H_{f,0}^\circ(NCO)$ being denoted as Methods (1)–(5), respectively.

$$\Delta H_{f,0}^\circ(NCO):\quad \text{Method (1)}\quad HNCO(\tilde{X}\,^1A') \rightarrow H(^2S)+NCO(^2\Pi), \quad (15)$$

$$(2)\quad HNCO(\tilde{X}\,^1A') \rightarrow H^+ + NCO^-, \quad (16)$$

$$(3)\quad N(^4S)+CO \rightarrow NCO(^2\Pi), \quad (17)$$

$$(4)\quad HCN+O(^3P) \rightarrow H(^2S)+NCO(^2\Pi), \quad (18)$$

$$(5)\quad NH(^3\Sigma^-)+CO \rightarrow H(^2S)+NCO(^2\Pi). \quad (19)$$

The computation of atomic and molecular total energies at various levels of theory included not only the species appearing in Reactions (13)–(19) but also the auxiliary molecules CH_2CO, $CH_2(^3B_1)$, $OH(^2\Pi)$, and N_2 for purposes of calibration. The data base of energetic predictions is given in Tables I and II here and in Tables III–V of our previous study[35] on HNCO and associated fragments. The empirically derived thermochemical quantities required to evaluate $\Delta H^\circ_{f,0}(\mathrm{HNCO})$, $\Delta H^\circ_{f,0}(\mathrm{HCN})$, and $\Delta H^\circ_{f,0}(\mathrm{NCO})$ from Reactions (13)–(19) are listed in Table III. The error estimates for all new thermochemical values ascertained here are to be interpreted as confidence intervals analogous to those arising from one standard deviation in a statistical analysis.

The one-particle Gaussian-orbital basis sets employed in this study are denoted as $\mathrm{DZ}(d,p)$, $\mathrm{QZ}(2d,2p)$, $\mathrm{QZ}(2d1f,2p1d)$, and $[13s8p6d4f,8s6p4d]$. In the first three cases, A in the designation $A(x,y)$ is descriptive of the underlying sp basis,[35] and x and y indicate the sets of polarization functions appended to the (C,N,O) atoms and the H atom, respectively. In the notation for the last basis set, the number of shells of each orbital type is explicitly given for the (C,N,O) and H atoms, in order. In the study of Reaction (16), the basis sets were augmented in an even-tempered manner with single sets of diffuse s and p functions on the (C,N,O) atoms, as signified by a suffix (+). For HNCO the various basis sets range in number of contracted Gaussian functions (CGFs) from 53 in the $\mathrm{DZ}(d,p)$ case to 343 in the $[13s8p6d4f,8s6p4d](+)$ set. The $[13s8p6d4f,8s6p4d]$ set for CH_2CO, which is comprised of 377 CGFs, is the largest basis set used here.

For carbon, nitrogen, and oxygen, the DZ sp basis involved the $(9s5p)$ Gaussian primitives of Huzinaga[46] and the $[4s2p]$ contractions of Dunning,[47] and the analogous hydrogen basis was a $(4s/2s)$ set in which the exponents were scaled by a factor of 1.2^2 as usual.[47] In the QZ case the (C,N,O) sp sets were Huzinaga–Dunning $(10s6p/5s4p)$ contractions,[48] while for hydrogen a $(6s/4s)$ contraction of the unscaled exponents of Huzinaga[46] was used, as tabulated by Allen and Schaefer.[49] In the $[13s8p6d4f,8s6p4d]$ case, the uncontracted sp primitives of van Duijneveldt[50] were employed.

The $\mathrm{DZ}(d,p)$ basis set was constructed from the DZ core by the addition of polarization functions to all atoms with exponents representative of optimal values for uncorrelated wave functions.[51] In contrast, these parameters in the QZ basis sets were the correlation-optimized exponents recommended by Dunning.[52] All exponents for the polarization functions of the $\mathrm{DZ}(d,p)$, $\mathrm{QZ}(2d,2p)$, and $\mathrm{QZ}(2d1f,2p1d)$ basis sets are explicitly given in Ref. 35. For the $[13s8p6d4f,8s6p4d]$ set, the polarization functions were selected as the Gaussian primitives of the atomic-natural-orbital (ANO) basis sets of Almlöf and Taylor.[53] The associated exponents are derived from the correlation-optimized[54] single exponents $\alpha_p(\mathrm{H})=1.0$, $\alpha_d(\mathrm{H,C,N,O})=(1.0,\ 0.72,\ 1.0,\ 1.28)$, and $\alpha_f(\mathrm{C,N,O})=(0.864,\ 1.2,\ 1.536)$ by preliminary splitting and subsequent even-tempered expansion with a geometric ratio of 2.5. In essence, the entire $[13s8p6d4f,8s6p4d]$ basis is identical to the uncontracted primitives within the ANO sets less the g and f manifolds for the (C,N,O) and H atoms, respectively. In the $\mathrm{DZ}(d,p)$ and $\mathrm{QZ}(2d,2p)$ cases, the d sets were comprised of six Cartesian components, whereas in the $\mathrm{QZ}(2d1f,2p1d)$ and $[13s8p6d4f,8s6p4d]$ cases the polarization sets involved only real combinations of the $l=2$ and 3 spherical harmonics.

Reference electronic wave functions were determined in this study by the single-configuration, self-consistent-field, restricted and unrestricted Hartree–Fock methods (RHF and UHF).[55–58] Dynamical electron correlation was accounted for by Møller–Plesset perturbation theory through fourth and occasionally fifth order [MP2, MP3, MP4(SDTQ), and MP5(SDTQ)],[59–62] by the coupled-cluster singles and doubles method (CCSD),[63–68] including the addition of a perturbative contribution from connected triple excitations [CCSD(T)],[69,70] and by Brueckner doubles theory (BD) with analogous corrections for connected triple and quadruple excitations [BD(T) and BD(TQ)].[71,72] For all open-shell molecules, the Møller–Plesset and Brueckner methods were implemented consistently with UHF reference wave functions; in contrast, all open-shell coupled-cluster energies were determined from the ordinary spin–orbital formula into which RHF orbitals were substituted.[73] Diagnostics ($\mathcal{T}_1$) for multireference character in electronic wave functions were computed as the Euclidean norm of the t_1(CCSD) amplitudes and compared to the recommended cutoff value of 0.02.[74] To maintain consistency among $\mathcal{T}_1$ values for both closed- and open-shell species, it was found necessary to invoke a definition for the open-shell diagnostic recently proposed by Jayatilaka and Lee,[75] viz.,

$$\mathcal{T}_1=2^{-1}N^{-1/2}\Bigg[\sum_{ia}(t_{i\alpha}^{a\alpha}+t_{i\beta}^{a\beta})^2+2\sum_{ua}(t_{u\alpha}^{a\alpha})^2 +2\sum_{iu}(t_{i\beta}^{u\beta})^2\Bigg]^{1/2}, \tag{20}$$

where the t_1 amplitudes are derived from the coupled-cluster formalism adopted here,[73] N is the number of active electrons, the indices i, u, and a denote doubly, singly, and unoccupied spatial orbitals, respectively, and a high-spin reference wave function with unpaired α rather than β electrons is assumed. In cases where MP5 calculations were possible, extrapolation of the MPn series was performed via shifted [1,2] Padé approximants to estimate the correlation energy in the MP∞ limit.[35,76–78] Selected full configuration interaction (FCI) energies for atomic fragments were also obtained to facilitate comparisons of CCSD(T), UMP5, and UMP∞ predictions.

In all electron correlation treatments, the $1s$ core orbital for each of the C, N, and O atoms was excluded from the active space. Likewise, in the $\mathrm{DZ}(d,p)$, $\mathrm{QZ}(2d,2p)$, and $\mathrm{QZ}(2d1f,2p1d)$ computations, the highest-lying $1s$ virtual orbital for each heavy atom was frozen in the correlation treatments, all of these orbitals lying higher than 20 a.u. in energy. In the $[13s8p6d4f,8s6p4d]$ MP2 procedures, several high-lying virtual orbitals with energies greater than 23 a.u. were kept unoccupied. The number of

TABLE I. Total energies (hartree) of relevant closed-shell molecules.[a–c]

HNCO	DZ(*d,p*)	MP5[−168.271 552], MP∞[−168.276 937], CCSD[−168.260 465], CCSD(T)[−168.278 954], BD[−168.258 614], BD(T)[−168.278 496], BD(TQ)[−168.278 026]
	QZ(2*d*1*f*,2*p*1*d*)	MP2[−168.421 547], MP3[−168.411 641], MP4[−168.457 009], CCSD[−168.417 651], CCSD(T)[−168.447 282] {$\mathcal{T}_1 = 0.018$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−167.843 611], MP2[−168.455 651]
	DZ(+)(*d,p*)	RHF[−167.800 821], MP2[−168.264 288], MP3[−168.258 252], MP4[−168.293 623], CCSD[−168.267 356], CCSD(T)[−168.286 394]
	QZ(+)(2*d*,2*p*)	RHF[−167.829 546], MP2[−168.375 749], MP3[−168.363 702], MP4[−168.408 765] CCSD[−168.371 907], CCSD(T)[−168.399 499]
	QZ(+)(2*d*1*f*,2*p*1*d*)	RHF[−167.835 195], MP2[−168.422 588], MP3[−168.412 521], MP4[−168.458 019], CCSD[−168.418 549], CCSD(T)[−168.448 249]
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*](+)	RHF[−167.843 619], MP2[−168.455 704]
NCO⁻	DZ(+)(*d,p*)	RHF[−167.246 851], MP2[−167.715 676], MP3[−167.703 818], MP4[−167.740 450], CCSD[−167.713 978], CCSD(T)[−167.733 082]
	QZ(+)(2*d*,2*p*)	RHF[−167.272 008], MP2[−167.825 362], MP3[−167.807 150], MP4[−167.854 760], CCSD[−167.816 297], CCSD(T)[−167.844 693]
	QZ(+)(2*d*1*f*,2*p*1*d*)	RHF[−167.276 821], MP2[−167.871 461], MP3[−167.855 386], MP4[−167.903 501], CCSD[−167.862 265], CCSD(T)[−167.892 862] {$\mathcal{T}_1 = 0.018$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*](+)	RHF[−167.284 671], MP2[−167.905 930]
CO	DZ(*d,p*)	MP5[−113.051 483], MP∞[−113.055 351], CCSD[−113.046 330], CCSD(T)[−113.056 579]
	QZ(2*d*,2*p*)	CCSD[−113.121 462], CCSD(T)[−113.137 879]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−112.782 658], MP2[−113.144 525], MP3[−113.139 736], MP4[−113.170 438], CCSD[−113.146 827], CCSD(T)[−113.164 433] {$\mathcal{T}_1 = 0.019$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−112.788 782], MP2[−113.166 838]
CH_2CO	QZ(2*d*1*f*,2*p*1*d*)	RHF[−151.789 086], MP2[−152.336 205], CCSD[−152.343 744], CCSD(T)[−152.370 747] {$\mathcal{T}_1 = 0.017$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−151.796 956], MP2[−152.368 311]
CO_2	DZ(*d,p*)	CCSD[−188.138 893], CCSD(T)[−188.156 303]
	QZ(2*d*,2*p*)[d]	RHF[−187.708 453], MP2[−188.275 091], MP3[−188.254 367], MP4[−188.302 497], CCSD[−188.264 530], CCSD(T)[−188.291 502]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−187.714 635], MP2[−188.324 576], MP3[−188.306 579], MP4[−188.355 018], CCSD[−188.314 575], CCSD(T)[−188.343 629] {$\mathcal{T}_1 = 0.018$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−187.724 542], MP2[−188.361 390]
HCN	DZ(*d,p*)	RHF[−92.888 849], MP2[−93.172 605], MP3[−93.174 678], MP4[−93.194 020], CCSD[−93.181 376], CCSD(T)[−93.192 611]
	QZ(2*d*,2*p*)	RHF[−92.908 496], MP2[−93.235 819], MP3[−93.233 937], MP4[−93.260 873], CCSD[−93.240 129], CCSD(T)[−93.257 048]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−92.910 961], MP2[−93.260 388], MP3[−93.259 183], MP4[−93.286 305], CCSD[−93.263 948], CCSD(T)[−93.282 164] {$\mathcal{T}_1 = 0.015$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−92.915 476], MP2[−93.278 800]
NH_3	DZ(*d,p*)	CCSD[−56.411 888], CCSD(T)[−56.415 752]
	QZ(2*d*,2*p*)	CCSD[−56.453 593], CCSD(T)[−56.460 763]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−56.221 183], MP2[−56.459 741], MP3[−56.470 523], MP4[−56.480 114], CCSD[−56.471 829], CCSD(T)[−56.479 780] {$\mathcal{T}_1 = 0.007$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−56.224 707], MP2[−56.473 989]
H_2O	DZ(*d,p*)	CCSD[−76.251 951], CCSD(T)[−76.255 145]
	QZ(2*d*,2*p*)	CCSD[−76.311 753], CCSD(T)[−76.318 978]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−76.062 136], MP2[−76.328 411], MP3[−76.331 763], MP4[−76.342 820], CCSD[−76.333 730], CCSD(T)[−76 341 765] {$\mathcal{T}_1 = 0.008$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−76.067 180], MP2[−76.347 088]
N_2	DZ(*d,p*)	RHF[−108.958 210], MP2[−109.262 179], MP3[−109.257 968], MP4[−109.279 229], MP5[−109.275 392], MP∞[−109.277 047], CCSD[−109.265 367], CCSD(T)[−109.276 405]
	QZ(2*d*,2*p*)	RHF[−108.983 437], MP2[−109.339 205], MP3[−109.330 231], MP4[−109.361 075]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−108.985 765], MP2[−109.364 219], MP3[−109.356 334], MP4[−109.387 051], CCSD[−109.362 161], CCSD(T)[−109.380 994] {$\mathcal{T}_1 = 0.013$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−108.992 621], MP2[−109.386 116]

[a] A complementary set of data is listed in Tables III and IV of Ref. 35. The QZ(2*d*1*f*,2*p*1*d*) MP*n* energies listed therein include supernumerary *s* functions in the Cartesian *d* polarization sets and thus are supplanted by the data tabulated here.

[b] The reference geometric structures for HNCO, NCO^-, CO, CO_2, NH_3, and H_2O are specified in the footnotes to Tables III and IV of Ref. 35. For CH_2CO, the QZ(2*d*1*f*,2*p*1*d*) CCSD(T) optimum geometry was employed, viz., r_e(C–H) = 1.0782 Å, r_e(C–C) = 1.3189 Å, r_e(C–O) = 1.1658 Å, and θ_e(H–C–H) = 121.89° (Ref. 37). For N_2, the experimental distance r_e(N–N) = 1.0977 Å was utilized from Ref. 38. For HCN, r_e(H–C) = 1.0655 Å and r_e(C–N) = 1.1532 Å were taken from experiment, Ref. 39.

[c] Selected diagnostics ($\mathcal{T}_1$) for multireference electronic character, as determined from the t_1[CCSD] amplitudes, are given in braces.

[d] The present QZ(2*d*,2*p*) data for CO_2 supercede those of Ref. 35, which were obtained at a slightly different geometry.

TABLE II. Total energies (hartree) of relevant open-shell fragments.[a–c]

NCO($^2\Pi$)	DZ(*d*,*p*)	UMP5[−167.598 782], UMP∞[−167.601 457], RCCSD[−167.587 644], RCCSD(T)[−167.605 125], UBD[−167.586 043], UBD(T)[−167.604 552], UBD(TQ)[−167.605 455]
	QZ(2*d*,2*p*)	RHF[−167.179 724], RCCSD[−167.692 263], RCCSD(T)[−167.718 457]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−167.185 008], UHF[−167.195 003], UMP2[−167.725 207], UMP3[−167.727 602], UMP4[−167.766 883], RCCSD[−167.736 126], RCCSD(T)[−167.764 399] {$S^2=0.836$, $\mathcal{T}_1=0.032$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−167.203 655], UMP2[−167.756 588]
N(^{4}S)	DZ(*d*,*p*)	RHF[−54.394 408], UHF[−54.397 584], UMP2[−54.466 738], UMP3[−54.480 232], UMP4[−54.482 129], RCCSD[−54.482 738], RCCSD(T)[−54.483 525], FCI[−54.483 715]
	QZ(2*d*,2*p*)	RHF[−54.398 786], UHF[−54.402 241], UMP2[−54.492 213], UMP3[−54.506 437], UMP4[−54.509 601], RCCSD[−54.508 423], RCCSD(T)[−54.510 228]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−54.398 689], UHF[−54.402 015], UMP2[−54.500 105], UMP3[−54.514 092], UMP4[−54.517 288], RCCSD[−54.515 503], RCCSD(T)[−54.517 897] {$S^2=3.756$, $\mathcal{T}_1=0.003$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−54.404 378], UMP2[−54.506 720]
NH($^3\Sigma^-$)	DZ(*d*,*p*)	UMP5[−55.099 227], UMP∞[−55.099 698], RCCSD[−55.097 743], RCCSD(T)[−55.099 503]
	QZ(2*d*,2*p*)	RHF[−54.975 142], RCCSD[−55.129 160], RCCSD(T)[−55.132 635]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−54.975 291], UHF[−54.983 059], UMP2[−55.122 273], UMP3[−55.138 490], UMP4[−55.143 538], RCCSD[−55.140 889], RCCSD(T)[−55.144 953] {$S^2=2.016$, $\mathcal{T}_1=0.005$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−54.986 106], UMP2[−55.131 811]
CH$_2$(^{3}B$_1$)	QZ(2*d*1*f*,2*p*1*d*)	RHF[−38.933 314], UHF[−38.938 897], UMP2[−39.058 084], RCCSD[−39.076 914], RCCSD(T)[−39.080 444] {$S^2=2.016$, $\mathcal{T}_1=0.011$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−38.940 762], UMP2[−39.065 856]
OH($^2\Pi$)	QZ(2*d*1*f*,2*p*1*d*)	RHF[−75.418 345], UHF[−75.423 187], UMP2[−75.626 911], UMP3[−75.638 712], UMP4[−75.645 158], RCCSD[−75.640 312], RCCSD(T)[−75.645 753] {$S^2=0.756$, $\mathcal{T}_1=0.007$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−75.427 780], UMP2[−75.642 457]
O(^{3}P)	DZ(*d*,*p*)	RHF[−74.800 583], UHF[−74.805 747], UMP2[−74.898 860], UMP3[−74.911 854], UMP4[−74.915 109], UMP5[−74.915 662], UMP∞[−74.915 811], RCCSD[−74.914 571], RCCSD(T)[−74.915 750], FCI[−74.915 963]
	QZ(2*d*,2*p*)	RHF[−74.808 072], UHF[−74.813 922], UMP2[−74.947 107], UMP3[−74.960 632], UMP4[−74.964 225], RCCSD[−74.962 450], RCCSD(T)[−74.965 049]
	QZ(2*d*1*f*,2*p*1*d*)	RHF[−74.808 712], UHF[−74.814 906], UMP2[−74.961 570], UMP3[−74.976 085], UMP4[−74.979 850], RCCSD[−74.977 462], RCCSD(T)[−74.980 602] {$S^2=2.008$, $\mathcal{T}_1=0.004$}
	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	UHF[−74.818 741], UMP2[−74.973 651]
H(^{2}S)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]	RHF[−0.499 995]

[a] A complementary set of data is listed in Table V of Ref. 35. The QZ(2*d*1*f*,2*p*1*d*) MP*n* energies listed therein are supplanted by the data tabulated here (n.b., footnote *a* of Table I above).

[b] The reference geometric structures for NCO and NH are the DZ(*d*,*p*) CISD optimum geometries appearing in Table I of Ref. 35. For CH$_2$($^3B_1$) and OH, the experimental structures of Refs. 40 and 38 were assumed; viz., r_e(C–H) = 1.077 Å and θ_e(H–C–H) = 134.0°; and r_e(O–H) = 0.96966 Å, respectively.

[c] In selected cases, the expectation value of S^2 for the UHF reference wave function and the diagnostic ($\mathcal{T}_1$) for multireference electronic character, as determined from the t_1[CCSD] amplitudes, are given in braces.

such orbitals attributable to the C, N, and O core regions was 18, 29, and 29, respectively, while six extra frozen virtuals arose from tight hydrogen primitives. The electronic structure computations reported here were performed by various implementations of the program packages PSI[79] and GAUSSIAN90 and 92.[80]

The reference geometric structures selected for the electronic structure computations are specified in the footnotes to Tables I and II and in the sources cited therein. In some cases precise empirical structures were used, and in other instances theoretical geometries were employed which are in excellent agreement with their experimental counterparts. The NCO radical constitutes an exception. By analysis of the $(00^01)\tilde{A}\,^2\Sigma^+-(00^10)\tilde{X}\,^2\Pi$ band of NCO isotopomers generated by flash photolysis of mixtures of HCN and ozonized oxygen, Misra and co-workers[14] extracted ground-state rotational constants for ^{14}NCO and ^{15}NCO which gave r_0(N–C) = 1.200(8) and r_0(C–O) = 1.206(8) Å. However, in the DZ(*d*,*p*) CISD reference structure assumed here, r_e(N–C) = 1.243 and r_e(C–O) = 1.171 Å. While the N–O separations agree to 0.008 Å in the two cases, the empirically derived geometry does not exhibit the bond asymmetry present in the theoretical structure. A re-evaluation of the QZ(2*d*1*f*,2*p*1*d*) CCSD(T) energy at the geometry of Misra *et al.*[14] actually increases this quantity by 1.04 kcal mol^{-1}. Moreover, by constraining the N–O separation to the empirical value and allowing the carbon atom to migrate on the QZ(2*d*1*f*,2*p*1*d*) CCSD(T) surface, a partially optimized, asymmetric structure is found at r_e(N–C) = 1.229 and r_e(C–O) = 1.177 Å which lies only 0.11 kcal mol^{-1} below the original theoretical reference-point energy. Finally, in a recent large-basis MR CI study,[81] the optimum parameters r_e(N–C) = 1.23 and r_e(C–O) = 1.19 were predicted. In brief, the empirical structure for NCO is somewhat questionable and is not adopted here. In this regard, it is note-

TABLE III. Gas-phase thermochemical data (kcal mol^{-1}) involved in the determination of $\Delta H^\circ_{f,0}$ of HNCO and NCO.

	$\Delta H^\circ_{f,0}$[a]	ZPVE[b]
$H(^2S)$	51.634(002)	0
$N(^4S)$	112.53(02)	0
$O(^3P)$	58.98(02)	0
CO	−27.20(04)	3.09
CO_2	−93.97(01)	7.24
$OH(^2\Pi)$	9.26(29)	5.28
H_2O	−57.10(01)	13.25
$NH(^3\Sigma^-)$	86.50(70)	4.64
N_2	0	3.36
NH_3	−9.30(10)	21.19
$CH_2(^3B_1)$	92.2(10)	10.62
CH_2CO	−12.1(10)	19.47
HCN	[+31.9(5)]	9.95
HNCO	[−27.5(5)]	13.37
$NCO(^2\Pi)$	[+31.4(5)]	6.16
NCO^-	[−51.7(5)]	6.64
IP(H)=313.588[c]	EA(NCO)=83.23(12)[d]	$D_0(CH_2\text{–}CO)=77.09(01)$[e]

[a] All values are experimental results except those appearing in brackets, which are the final proposals from the current investigation. The source for the H, N, O, CO, CO_2, OH, H_2O, NH_3, and CH_2 data is Ref. 26. The heat of formation of imidogen is based on the N–H bond energy recommended in Ref. 41. The value for CH_2CO results by appending the tabulated dissociation energy, $D_0(CH_2\text{–}CO)$, to the heat of formation of $CH_2(^3B_1)$.

[b] The zero-point vibrational energies (ZPVEs) for most species were evaluated using anharmonic molecular force fields. See the text for details.

[c] Reference 42.

[d] Reference 43.

[e] Evaluated from the spin-allowed fragmentation energy of Ref. 44 and the singlet–triplet splitting of methylene. See Ref. 45.

worthy that Bradforth and co-workers[43] have recently obtained a structure for NCO^- by appending geometric shifts [$\delta r(N\text{–}C) = -0.034(10)$ and $\delta r(C\text{–}O) = 0.051(10)$ Å] derived from a Franck–Condon analysis of the photoelectron spectrum of this anion to the structure of the free radical in question. Because the corresponding shifts [$\delta r(N\text{–}C) = -0.051$ and $\delta r(C\text{–}O) = 0.063$ Å] in the DZ(d,p) CISD reference structures assumed here[82] generally support the Franck–Condon analysis, the discrepancy observed for the structure of NCO is translated into a similar one for NCO^-. This disparity for NCO and NCO^- notwithstanding, it is expected that the effect of differential errors in reference geometries on the thermochemical results reported here is less than 0.2 kcal mol^{-1} in all cases.

The zero-point vibrational energies (ZPVEs) utilized in this study (Table III) were generally evaluated using empirically derived fundamental frequencies and anharmonic molecular force fields in order to maximize accuracy, as described in our previous work.[35] Requisite spectroscopic constants were taken from the following sources: CO,[38] CO_2,[83] OH,[38] H_2O,[84] NH,[38] N_2,[38] HCN,[85] NH_3,[86–88] and HNCO.[35] The ZPVE of NCO derived previously[35] was modified slightly by using $\chi_{11} = -3$ cm^{-1} rather than -64 cm^{-1},[11] in accord with the well-established anharmonic constants of CO_2.[83] The ZPVE computation for NCO^- utilized ν_1 and ν_2 values from a KBr-matrix Raman investigation,[89] a high-precision, gas-phase infrared ν_3 fundamental,[90] and χ_{ij} constants determined in a KI-matrix infrared study.[91] For $CH_2(^3B_1)$ the results of a variational vibrational analysis on an ANO[$5s4p3d2f1g,3s2p1d$] MR CI surface[92] were assumed. Finally, the ZPVE of the auxiliary CH_2CO molecule was estimated by taking one-half the sum of the observed fundamental frequencies[93] and multiplying by a factor of 1.014, as suggested by the known anharmonic force fields of formaldehyde and carbon dioxide.

FOCAL-POINT METHOD AND BOND ADDITIVITY CORRECTIONS

The homolytic cleavage of chemical bonds engenders a large differential correlation effect on dissociation energies which can only be reliably recovered by rigorous correlation treatments with large one-particle basis sets. In view of this widespread observation, the principal technique employed here to derive thermochemical predictions entailed the direct computation of QZ($2d1f,2p1d$) CCSD(T) reaction energies to which QZ($2d1f,2p1d$) $\rightarrow$[$13s8p6d4f,8s6p4d$] MP2 shifts were appended as correlated, basis set incompleteness corrections. This procedure is referred to as the focal-point (fp) level of theory in the current study. The convergence behavior of the various entries in the reaction energy tables for Eqs. (13)–(19) yields compelling evidence that the focal-point method provides an excellent approximation to full [$13s8p6d4f,8s6p4d$] CCSD(T) results (see Tables V–XI below). Rapid convergence with respect to basis set augmentation of the higher-order correlation increments for the reaction energy is a salient feature of all reactions investigated here, an occurrence which was noted in earlier studies[35,94] in our laboratory. To facilitate the effective use of this phenomenon, the higher-order correlation data are cast into two parallel sequences for each basis set, viz., MP3$\rightarrow$MP4$\rightarrow$MP5 and MP3$\rightarrow$CCSD$\rightarrow$CCSD(T). The construction of these parallel sequences is broadly consistent with the theoretical foundations underpinning the predictions; e.g., the CCSD(T) method is fully correct to fourth order and partially correct to fifth order in perturbation theory, while also including some correlation terms to infinite order.[69,71,95,96] However, the molecular orbitals in the coupled-cluster and MPn treatments of all open-shell species were not identical (*vide supra*), and thus in general the two correlation sequences should be viewed foremost as complementary arithmetic perspectives on the data rather than a rigorous comparison of alternate approaches to the full configuration interaction limit.

In Table IV data are shown for prototypical bond dissociation energies which allow the fp method to be calibrated. For the single bonds in water and ammonia, the fp technique gives remarkably consistent predictions which are below experiment by only 0.8 to 1.1 kcal mol^{-1}. The energies required to break the C═O and C═C double bonds in carbon dioxide and ketene to yield ground state fragments are underestimated to a somewhat larger extent, viz., 3.76 and 2.59 kcal mol^{-1}, respectively. The results for the analogous fragmentation of isocyanic acid are also consistent with discrepancies of this magnitude, although uncertainty in the experimental dissociation energy hinders

TABLE IV. Bond additivity corrections (BACs) for focal-point level of theory.[a]

	δ(corr)[b]	δ(basis)[c]	ΔE_e[fp]	ΔE_e[expt][d]	BAC[e]
Single bonds					
$OH(^2\Pi) \rightarrow O(^3P) + H(^2S)$	1.55	2.13	105.79	106.62(30)	0.83(30)
$\frac{1}{2}[H_2O \rightarrow O(^3P) + 2H(^2S)]$	1.59	2.03	115.38	116.29(02)	0.91(02)
$NH(^3\Sigma^-) \rightarrow N(^4S) + H(^2S)$	1.05	1.80	81.57	82.40(70)	0.83(70)
$\frac{1}{3}[NH_3 \rightarrow N(^4S) + 3H(^2S)]$	1.16	1.56	98.21	99.32(03)	1.11(03)
$HNCO \rightarrow H(^2S) + NCO(^2\Pi)$	0.85	1.68	116.48		[1.1]
Double bonds					
$CO_2 \rightarrow O(^3P) + CO$	5.21	1.52	126.14	129.90(05)	3.76(05)
$HNCO \rightarrow NH(^3\Sigma^-) + CO$	4.99	1.41	87.94	92.47(90)[f]	4.53(90)
$CH_2CO \rightarrow CH_2(^3B_1) + CO$	3.68	1.27	80.25	82.84(10)	2.59(10)
$NCO(^2\Pi) \rightarrow N(^4S) + CO$	5.19	1.54	53.04		[3.8]
Triple bonds					
$N_2 \rightarrow 2N(^4S)$	8.81	5.44	222.06	228.41(01)	6.35(01)

[a] All values in kcal mol^{-1}.

[b] Higher-order correlation shift in reaction energy, QZ(2*d*1*f*,2*p*1*d*)CCSD→QZ(2*d*1*f*,2*p*1*d*) CCSD(T).

[c] Basis set augmentation shift in reaction energy, QZ(2*d*1*f*,2*p*1*d*)MP2→[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] MP2.

[d] Evaluated from the data listed in Table III.

[e] Observed bond additivity corrections for focal-point level of theory. Assumed values are shown in brackets.

[f] Uncertainty includes an error estimate of ±0.5 kcal mol^{-1} for the heat of formation of HNCO.

the use of this reaction as a primary standard. The fp level of theory applied to the homolytic cleavage of the prodigious triple bond in N_2 predicts a dissociation energy 6.35 kcal mol^{-1} less than the observed value. In summary, these results show that for bonds among C, N, and O atoms, the fp method fails to recover roughly 2 kcal mol^{-1} per bond, whereas for bonds of these atoms to hydrogen this deficiency is only 1 kcal mol^{-1}.

Bond additivity corrections (BACs) can be selected from the results in Table IV to improve the thermochemical predictions at the fp level for transformations which involve homolytic bond cleavage and/or formation, specifically, Reactions (15), (17), (18), and (19). Such BACs account not only for the balance of residual basis set and valence correlation errors but also for other small but perhaps significant effects such as core–valence and core–core electron correlation, which is known to be a few tenths of a kcal mol^{-1} for bond dissociations in similar systems.[97,98] An important trend revealed in Table IV is that the δ(corr) shifts, defined here as the coupled-cluster (T) corrections with the QZ(2*d*1*f*,2*p*1*d*) basis set, are generally indicative of the corresponding errors in the bond dissociation energies. For example, the δ(corr) values for the multiple-bond fragmentations in CH_2CO, CO_2, and N_2 are 3.68, 5.21, and 8.81 kcal mol^{-1}, as compared to the respective bond-energy underestimations of 2.59, 3.76, and 6.35 kcal mol^{-1}. This phenomenon can be used to aid the selection of appropriate bond additivity corrections.

For Reaction (15) a BAC of 1.1 kcal mol^{-1} is chosen by calibration on the precisely known atomization energy of NH_3. For the N=C bond cleavage involved in the reverse of Reaction (17), the best available choice for the BAC is arguably the 3.8 kcal mol^{-1} value given by the $CO_2 \rightarrow CO + O(^3P)$ fragmentation, which exhibits δ(corr) and δ(basis) shifts commensurate with those for the analogous NCO dissociation and yields a precise result intermediate in the range of tabulated values. Finally, because Reactions (18) and (19) can be decomposed into steps involving formation of the C=O or N=C bond in NCO and cleavage of a C–H or N–H bond, the BAC is chosen in both cases as the difference (-2.7 kcal mol^{-1}) between the correction terms for Reactions (15) and (17). The use of more elaborate bond additivity schemes to facilitate the computation of accurate heats of formation has been extensively developed and widely applied by Melius and collaborators[99–102] at the 6–31G(*d,p*) MP4 level of theory. The restricted system size here and considerable improvement in the underlying level of theory provide a large reduction in the BACs of the fp procedure relative to the standard BAC-MP4 method. For example, the 6–31G(*d,p*) UMP4 method underestimates the known atomization energies of NH_3 and N_2 by 25.3 and 23.7 kcal mol^{-1}, respectively,[103] whereas the fp level of theory in the current study yields corresponding errors of only 3.3 and 6.4 kcal mol^{-1}. Of the numerous schemes in common usage for computing heats of formation, only the G2 method of Pople and co-workers[104] approaches the rigor of the *ab initio* methods applied here.

HEAT OF FORMATION OF HNCO AND HCN

The revision of the heat of formation of HNCO via Reaction (13) is detailed in Table V. Because Reaction (13) is not only isogyric but also comprised of isoelectronic pairs of reactants and products, differential correlation effects are small,[35] and bond additivity corrections are unnecessary. While the [13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] δ[MP2] contribution to the reaction energy is -3.68 kcal mol^{-1}, the net higher-order correlation effect is less than 0.25 kcal mol^{-1} in all cases. The more highly polarized product species are systematically favored with basis set enlargement due to both the aggrandizement of the δ[MP2] term and modest reductions of ΔE_e[RHF]. The focal-point level of theory provides ΔE_e[fp]=20.45 kcal mol^{-1} for the reac-

TABLE V. Evaluation of $\Delta H^\circ_{f,0}$(HNCO).[a]

$CO_2+NH_3\rightarrow HNCO+H_2O$	DZ(*d,p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[RHF]	24.95	24.44	24.49	24.13
δ[MP2]	−0.91	−2.65	−2.93	−3.68
δ[MP3]	−0.77	−0.44	−0.41	[−0.41]
(δ[MP4],δ[CCSD])	(+1.25,+0.81)	(+1.05,+0.80)	(+1.00,+0.83)	[+0.83]
δ[CCSD(T)]	−0.26	−0.38	−0.42	[−0.42]
ΔE_e(corr)	23.82	21.77	21.56	[20.45]

$\Delta E_0=\Delta E_e[\text{fp}]+\Delta[\text{ZPVE}]=20.45-1.81=18.64$ kcal mol^{-1}
$\Delta H^\circ_{f,0}(\text{HNCO})=\Delta E_0+\Delta H^\circ_{f,0}(CO_2)+\Delta H^\circ_{f,0}(NH_3)-\Delta H^\circ_{f,0}(H_2O)$
$=18.64-93.97-9.30+57.10=-\mathbf{27.5}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}. The symbol δ denotes the *increment* in the reaction energy (ΔE_e) relative to the preceding level of theory. In evaluating these contributions, the MP3→CCSD→CCSD(T) higher-order correlation sequence is constructed as an alternate to the MP*n* series. For the [13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] basis set, the increments in brackets are assumed values based on the QZ(2*d*1*f*,2*p*1*d*) CCSD(T) predictions. The estimated [13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] net reaction energy, ΔE_e(corr), is equivalent to the energy change, ΔE_e[fp], predicted at the focal-point (fp) level of theory described in the text.

tion, which translates into $\Delta H^\circ_{f,0}(\text{HNCO})=-27.5(5)$ kcal mol^{-1}. The latter result is 1.4 kcal mol^{-1} lower than our previous value[35] due to basis set and higher-order correlation shifts of −0.8 and −0.6 kcal mol^{-1}, respectively. The BAC-MP4 result[105] of −27.9(31) kcal mol^{-1} is thereby confirmed by *ab initio* computations at much higher levels of theory without the aid of empirical corrections. The newly proposed heat of formation of HNCO shows that the experimental value of Spiglanin *et al.* ($-24.9^{+0.7}_{-2.8}$ kcal mol^{-1})[28] should be shifted to near the lower limit of the stated error bars. Cogent arguments[35] can be made to rationalize this modification.

The determination of $\Delta H^\circ_{f,0}$(NCO) from Reaction (18) is predicated on the precise knowledge of $\Delta H^\circ_{f,0}$(HCN), which is listed in the JANAF thermochemical tables[26] as 32.4±2.0 kcal mol^{-1}. In order to refine this quantity, the results collected in Table VI were generated for Reaction (14). The theoretical contributions to the reaction energy are not as strongly convergent as for Reaction (13); nevertheless, a reliable fp result is readily obtained because the δ[CCSD] and δ[CCSD(T)] terms are both small and insensitive to basis set. From $\Delta E_e[\text{fp}]=12.39$ kcal mol^{-1}, $\Delta H^\circ_{f,0}(\text{HCN})=31.9(5)$ kcal mol^{-1} is extracted for use in the Method (4) evaluation of $\Delta H^\circ_{f,0}$(NCO). The BAC-MP4 value[105] for $\Delta H^\circ_{f,0}$(HCN) happens to be identical to this result despite a larger inherent uncertainty. It is thus apparent that the error bars on the JANAF recommendation for the heat of formation of HCN should be reduced significantly.

HEAT OF FORMATION OF NCO

Independent evaluations of the heat of formation of the cyanato radical by Methods (1)–(5) based on Reactions (15)–(19) are summarized in Tables VII–XI, respectively.

Method (1)

Previously it was noted that the DZ(*d,p*)-QZ(2*d*1*f*,2*p*1*d*) data for the MP2–MP4 methods as applied to the N–H bond cleavage in HNCO are quite similar to the analogous predictions for the O–H bond dissociation energy in H_2O.[35] The DZ(*d,p*) δ[MP5] correlation contribution to the N–H bond energy in Table VII shows that such a comparison is quite misleading, because the magnitude of this quantity (−5.16 kcal mol^{-1}) is more than 4 kcal mol^{-1} larger than in the H_2O case. This anomalous higher-order correction originates in the electronic structure of NCO, which is the only species in Tables I and II whose $\mathcal{T}_1$ diagnostic (0.032) for multireference electronic character is significantly greater than the generally ac-

TABLE VI. Evaluation of $\Delta H^\circ_{f,0}$(HCN).[a]

$CO+NH_3\rightarrow HCN+H_2O$	DZ(*d,p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[RHF]	19.88	19.64	19.29	19.35
δ[MP2]	−7.23	−8.73	−9.58	−9.98
δ[MP3]	+1.94	+2.61	+2.41	[+2.41]
(δ[MP4],δ[CCSD])	(+2.50,+1.03)	(+1.51,+1.02)	(+1.33,+1.04)	[+1.04]
δ[CCSD(T)]	−0.20	−0.35	−0.43	[−0.43]
ΔE_e(corr)	15.42	14.19	12.73	[12.39]

$\Delta E_0=\Delta E_e[\text{fp}]+\Delta[\text{ZPVE}]=12.39-1.08=11.31$ kcal mol^{-1}
$\Delta H^\circ_{f,0}(\text{HCN})=\Delta E_0+\Delta H^\circ_{f,0}(CO)+\Delta H^\circ_{f,0}(NH_3)-\Delta H^\circ_{f,0}(H_2O)$
$=11.31-27.20-9.30+57.10=+\mathbf{31.9}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}. See footnote a of Table V.

TABLE VII. Evaluation of $\Delta H^\circ_{f,0}$(NCO) by Method (1).[a]

$HNCO(\tilde{X}\,^1A') \rightarrow H(^2S) + NCO(\tilde{X}\,^2\Pi)$				
	DZ(*d*,*p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[UHF]	88.06	87.60	87.67	87.83
δ[MP2]	+31.03	+33.90	+35.57	+37.09
δ[MP3]	−7.20	−7.74	−7.72	[−7.72]
(δ[MP4],δ[CCSD])	(+3.17,−1.96)	(+3.85,−1.53)	(+3.82,−1.57)	[−1.57]
(δ[MP5],δ[CCSD(T)])	(−5.16,+0.63)	(na,+0.84)	(na,+0.85)	[+0.85]
ΔE_e(corr)	(109.90,110.56)	(na,113.07)	(na,114.80)	[116.48]
ΔE_e[UBD(T),UBD(TQ)]	(110.63,109.77)			

$\Delta E_0(1) = \Delta E_e[\mathrm{fp}] + \mathrm{BAC} + \Delta[\mathrm{ZPVE}] = 116.5 + 1.1 - 7.2 = 110.4$ kcal mol^{-1}

$\Delta H^\circ_{f,0}(\mathrm{NCO};1) = \Delta E_0(1) + \Delta H^\circ_{f,0}(\mathrm{HNCO}) - \Delta H^\circ_{f,0}(\mathrm{H}) = 110.4 - 27.53 - 51.63 = +\mathbf{31.2}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}; na=not available. See footnote a of Table V.

cepted cutoff value of 0.02.[74] Likewise, the relatively large spin contamination (0.084) in the QZ(2*d*1*f*,2*p*1*d*) UHF reference wave function for NCO is the only one in Table II greater than 0.05 atomic units.

The effect of the multireference character of NCO on the N–H bond energy of isocyanic acid is more precisely evaluated by computing the Brueckner orbitals of the cyanato radical and determining the BD(T) and BD(TQ) dissociation energies with the DZ(*d*,*p*) basis set. As seen in Table VII, the DZ(*d*,*p*) CCSD(T), BD(T), BD(TQ), and MP5 bond energies lie in the narrow interval 110.2±0.5 kcal mol^{-1}. Moreover, the BD(T) result differs from its CCSD(T) counterpart by only 0.07 kcal mol^{-1}, even though the orbitals are optimized in the correlation treatment in the former case. These observations bolster confidence that the CCSD(T) level of theory, from which the focal-point predictions are computed, accounts for the nondynamical correlation problem in NCO sufficiently well that the small BAC for N–H bond cleavage derived from the NH_3 atomization process is applicable. By appending this BAC term and the relevant ZPVE contribution to ΔE_e[fp] (116.48 kcal mol^{-1}) for Reaction (15), D_0(H–NCO) = 110.4 kcal mol^{-1} is obtained, which is still within the error bars of our previous *ab initio* estimate (112±2 kcal mol^{-1}) but 2.6 kcal mol^{-1} below the value arising from the photodissociation threshold of Okabe.[25] In this respect the more recent empirical result of Shobatake,[106] D_0(H–NCO) = 111 kcal mol^{-1}, is favored over the original dissociation energy of Okabe. Finally, the heat of formation of NCO given by Method (1) is 31.2 kcal mol^{-1}, a revision downward of slightly more than 4 kcal mol^{-1} from our previous recommendation. The apparent error in the assumed N–H bond energy of Okabe accounts for 2.6 kcal mol^{-1} of this revision while the source of the remaining portion is the 1.4 kcal mol^{-1} lowering of the recommended $\Delta H^\circ_{f,0}$(HNCO) value.

Method (2)

Reaction (16) allows $\Delta H^\circ_{f,0}$(NCO) to be determined from an isogyric process *without bond additivity corrections*. This heterolytic cleavage was utilized previously[35] as an alternate means of ascertaining D_0(H–NCO), but a 4.6 kcal mol^{-1} uncertainty in the available experimental electron affinity of the NCO radical prevented the determination of a precise N–H bond energy. However, Bradforth and co-workers[43] have very recently measured EA(NCO) = 83.23(12) kcal mol^{-1} via time-of-flight photoelectron spectroscopy of jet cooled cyanate ions, which actualizes Reaction (16) as a preferred theoretical approach in the resolution of the $\Delta H^\circ_{f,0}$(NCO) controversy. The anticipated mitigation of the differential correlation effect for Reaction (16) relative to Reaction (15) is indeed manifested in Table VIII, where the RHF method is seen to predict the proton affinity to better than 1%. The basis sets appearing in the table include diffuse atomic orbitals in each case to allow the convergence behavior of individual contributions to the reaction energy to be clearly exposed.

TABLE VIII. Evaluation of $\Delta H^\circ_{f,0}$(NCO) by Method (2).[a]

$HNCO(\tilde{X}\,^1A') \rightarrow H^+ + NCO^-$				
	DZ(+)(*d*,*p*)	QZ(+)(2*d*,2*p*)	QZ(+)(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*](+)
ΔE_e[RHF]	347.62	349.86	350.39	350.75
δ[MP2]	−3.36	−4.49	−4.55	−5.79
δ[MP3]	+3.65	+3.87	+3.77	[+3.77]
(δ[MP4],δ[CCSD])	(−0.79,−0.66)	(−1.60,−0.59)	(−1.64,−0.53)	[−0.53]
δ[CCSD(T)]	−0.04	−0.50	−0.56	[−0.56]
ΔE_e(corr)	347.21	348.15	348.51	[347.64]

$\Delta E_0(2) = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] = 347.6 - 6.7 = 340.9$ kcal mol^{-1}

$\Delta H^\circ_{f,0}(\mathrm{NCO};2) = \Delta E_0(2) - \mathrm{IP(H)} + \mathrm{EA(NCO)} + \Delta H^\circ_{f,0}(\mathrm{HNCO}) - \Delta H^\circ_{f,0}(\mathrm{H})$
$= 340.9 - 313.59 + 83.23 - 27.53 - 51.63 = +\mathbf{31.4}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}. See footnote a of Table V.

TABLE IX. Evaluation of $\Delta H^\circ_{f,0}$(NCO) by Method (3).[a]

$N(^4S)+CO \rightarrow NCO(\tilde{X}\,^2\Pi)$	DZ(*d*,*p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[UHF]	−2.46	−4.43	−6.48	−6.59
δ[MP2]	−37.25	−39.63	−44.08	−45.51
δ[MP3]	+3.39	+4.98	+4.27	[+4.27]
(δ[MP4],δ[CCSD])	(−2.22,−0.44)	(−3.00,−0.06)	(−3.38,−0.02)	[−0.02]
(δ[MP5],δ[CCSD(T)])	(−1.5[b],−4.04)	(na,−5.01)	(na,−5.19)	[−5.19]
ΔE_e(corr)	(−40.0,−40.80)	(na,−44.15)	(na,−51.50)	[−53.04]

$\Delta E_0(3)=\Delta E_e[\text{fp}]+\text{BAC}+\Delta[\text{ZPVE}]=-53.0-3.8+3.1=-53.7$ kcal mol^{-1}

$\Delta H^\circ_{f,0}(\text{NCO},3)=\Delta E_0(3)+\Delta H^\circ_{f,0}(\text{N})+\Delta H^\circ_{f,0}(\text{CO})=-53.7+112.53-27.20=+\mathbf{31.6}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}; na=not available. See footnote a of Table V.

[b] Limitations of the GAUSSIAN92 package prevented the direct evaluation of the MP5 energy of $N(^4S)$, which is estimated here as the corresponding CCSD(T) energy. In the case of $O(^3P)$, this approximation is accurate to 0.055 kcal mol^{-1}, and both the MP5 and CCSD(T) energies differ by less than 0.2 kcal mol^{-1} from the FCI value (see Table II).

While the first set of appended diffuse functions serves to reduce the proton affinity of NCO$^-$ by 2.0–3.5 kcal mol^{-1} in computations with the QZ basis sets,[35] a second even-tempered extension of the diffuse *sp* space changes the proton affinity only on the order of 0.01 kcal mol^{-1}. Systematic improvement of the valence basis set establishes a trend of increasing ΔE_e[RHF] values which are largely compensated by shifts in the δ[MP2] contributions. The δ[MP3] term of ca. +3.8 kcal mol^{-1} is remarkably insensitive to basis set variations and is partially balanced by a −1 kcal mol^{-1} higher-order correlation effect. The fp result, $\Delta E_e[\text{fp}]=347.64$ kcal mol^{-1}, yields a final, ZPVE-corrected proton affinity of 340.9 kcal mol^{-1}, which is equivalent to a bond enthalpy of $DH_{298}(H^+\text{–}NCO^-)=342.0$ kcal mol^{-1}. By comparison, Wight and Beauchamp[107] observed a corresponding bond enthalpy of 344.7±2 kcal mol^{-1} by the proton abstraction of HCO_2^- with HNCO in an ion cyclotron resonance cell, whereas Bradforth *et al.*[43] calculated $DH_{298}(H^+\text{–}NCO^-)=343.2\pm1$ kcal mol^{-1} from the HNCO photodissociation threshold of Shobatake[106] combined with their electron affinity of the NCO radical. On the basis of the observed ionization potential of the H atom and the electron affinity of NCO, a final $\Delta H^\circ_{f,0}$(NCO) value of 31.4 kcal mol^{-1} is obtained according to Method (2).

Method (3)

By employing Reaction (17) in the evaluation of $\Delta H^\circ_{f,0}$(NCO), the use of thermochemical cycles involving the heat of formation of HNCO is averted. In such a direct theoretical probe of the N═C multiple bond of NCO, the complete recovery of the correlation contribution to the bond energy is expected to be laborious. The merit of the fp approach to this problem augmented by an appropriate BAC is clearly apparent in Table IX. Note therein that the QZ(2*d*,2*p*)→QZ(2*d*1*f*,2*p*1*d*) augmentation enhances the net MP2 binding energy by a full 6.5 kcal mol^{-1}, but the concomitant changes in the δ[MP3] and coupled-cluster terms are only 0.71 and less than 0.2 kcal mol^{-1}, respectively. Again the evidence is compelling that the fp method gives predictions which closely approximate [13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] CCSD(T) results. The basis set incompleteness error in the [13*s*8*p*6*d*4*f*,8*s*6*p*4*d*] δ[MP2] term, while still substantial, is accounted for by the BAC of 3.8 kcal mol^{-1} for Reaction (17). The central concern is thus the extent of convergence of the correlation series in Table IX, especially considering the significant multireference character of NCO. Germane to this issue is the agreement of the DZ(*d*,*p*) MP5 and CCSD(T) dissociation energies to 0.8 kcal mol^{-1}. Moreover, from the FCI energy of $N(^4S)$ and the MP∞ extrapolations for CO and NCO (n.b., footnote b of Table IX), a limiting DZ(*d*,*p*) ΔE_e value of −39.2 kcal mol^{-1} is estimated, which deviates from the CCSD(T) prediction by only 1.6 kcal mol^{-1}. Such remaining errors are incorporated into the BAC to the degree that the CCSD(T) method provides a consistent level of treatment for both Reaction (17) and the analogous CO_2 fragmentation from which the empirical correction is derived. The aforementioned near equivalence of the coupled-cluster (*T*) contributions to these bond energies, i.e., the associated δ(corr) entries in Table IV, suggests that this consistency criterion is indeed satisfied. The final bond energy derived by Method (3) is D_0(N–CO) =53.7 kcal mol^{-1}, from which $\Delta H^\circ_{f,0}$(NCO)=31.6 kcal mol^{-1} accrues. In the simulations of Cyr *et al.*[36] of the observed time-of-flight spectra for NCO free radical photodissociation, D_0(N–CO)=54.9 kcal mol^{-1} was found to be optimal, in good agreement with the Method (3) prediction here.

Method (4)

Reaction (18) involves a theoretical probe of the C═O multiple bond in NCO as a pathway to $\Delta H^\circ_{f,0}$(NCO). In this sense it is both complementary and analogous to the investigation of the C═N bond of NCO via Reaction (17), except that a hydrogen atom is included in the transformation to avoid the necessity of treating the egregious correlation problem for the CN radical.[108] The key points in the analysis of the data in Table X have been highlighted in the discussion of Methods (1)–(3). It is noteworthy that the convergence properties of the data for Reaction (18)

TABLE X. Evaluation of $\Delta H^\circ_{f,0}$(NCO) by Method (4).[a]

$HCN+O(^3P)\rightarrow H(^2S)+NCO(\tilde{X}\,^2\Pi)$	DZ(*d*,*p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[UHF]	23.35	20.68	19.41	19.18
δ[MP2]	−20.65	−19.57	−21.41	−21.77
δ[MP3]	+5.59	+7.03	+6.85	[+6.85]
(δ[MP4],δ[CCSD])	(−4.11,−1.60)	(−5.19,−1.63)	(−5.27,−1.50)	[−1.50]
δ[CCSD(T)]	−3.18	−4.19	−4.34	[−4.34]
ΔE_e(corr)	3.51	2.32	−0.99	[−1.58]

$\Delta E_0(4)=\Delta E_e[\mathrm{fp}]+\mathrm{BAC}+\Delta[\mathrm{ZPVE}]=-1.58-2.7-3.79=-8.1$ kcal mol^{-1}

$\Delta H^\circ_{f,0}(\mathrm{NCO};4)=\Delta E_0(4)-\Delta H^\circ_{f,0}(\mathrm{H})+\Delta H^\circ_{f,0}(\mathrm{HCN})+\Delta H^\circ_{f,0}(\mathrm{O})$

$=-8.1-51.634+31.91+58.98=+\mathbf{31.2}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}. See footnote a of Table V.

are generally better than observed for Reaction (17). In particular, the coupled-cluster (T) correction to the reaction energy is diminished by ca. 1 kcal mol^{-1}, because its magnitude appears to parallel the difference of the analogous corrections for the two reactions which provide the BAC for Eq. (18). This phenomenon is documented by the entries in Table IV. The focal-point level of theory gives $\Delta E_e[\mathrm{fp}]=-1.58$ kcal mol^{-1} for Reaction (18), whence $\Delta H^\circ_{f,0}(\mathrm{NCO})=31.2$ kcal mol^{-1} is ascertained using our refined value for $\Delta H^\circ_{f,0}$(HCN).

Method (5)

The evaluation of $\Delta H^\circ_{f,0}$(NCO) by Reaction (19) can be viewed as a variant of Method (1) in which the fragmentation reaction of isocyanic acid to triplet imidogen and carbon monoxide has been employed to deflate $\Delta H^\circ_{f,0}$(HNCO) from the thermochemical derivation. The general features exhibited by the reaction energy contributions in Table XI are the same as those observed in the preceding tabulations, the one for Method (4) in particular. To wit, the higher-order correlation terms show good basis set convergence; the DZ(*d*,*p*) MP5, MP∞, and CCSD(T) reaction energies, 34.07, 35.11, and 33.46 kcal mol^{-1}, respectively, lie in a narrow 1.65 kcal mol^{-1} interval; and the coupled-cluster (T) correction with the QZ(2*d*1*f*,2*p*1*d*) basis set (−4.14 kcal mol^{-1}) is remarkably close to the difference of the δ(corr) values for the pertinent calibration reactions. The fp reaction energy of 28.53 kcal mol^{-1} gives rise to $\Delta H^\circ_{f,0}(\mathrm{NCO})=31.9$ kcal mol^{-1}. The shift of this result from the Method (1) value is precisely the differential error of the assumed BAC for N=C bond fragmentation in the NCO and HNCO cases, as revealed in Table IV.

In summary, the five independent methods implemented in the determination of the heat of formation of the cyanato radical yield a set of $\Delta H^\circ_{f,0}$(NCO) values which are in remarkable agreement: (1) 31.2, (2) 31.4, (3) 31.6, (4) 31.2, and (5) 31.9 kcal mol^{-1}. While the uncertainty in the individual predictions is approximately 1 kcal mol^{-1}, the consistency among them leads to a more precise recommendation of $\Delta H^\circ_{f,0}(\mathrm{NCO})=31.4(5)$ kcal mol^{-1}. This definitive result resolves the controversy over the heat of formation of NCO in favor of the value (30.5±1 kcal mol^{-1}) obtained by Cyr *et al.*[36] from time-of-flight spectroscopy of the products of NCO free radical photodissociation. Consequently, many of the arguments proffered by these investigators to establish the veracity of their $\Delta H^\circ_{f,0}$(NCO) deduction in light of earlier, conflicting experimental conclusions are confirmed. The current thermochemical revisions also reveal that the BAC-MP4 prediction[109] of $\Delta H^\circ_{f,0}(\mathrm{NCO})=32.1\pm4.8$ kcal mol^{-1}, which contains a sizeable correction for spin contamination in the NCO reference wave function, is more accurate than previously thought. Finally, a previous tabulation[35] of energetic data for CHNO isomers and associated fragments can be updated based on the conclusions of this study, as provided in Fig. 1.

TABLE XI. Evaluation of $\Delta H^\circ_{f,0}$(NCO) by Method (5).[a]

$NH(\tilde{X}\,^3\Sigma^-)+CO\rightarrow H(^2S)+NCO(\tilde{X}\,^2\Pi)$	DZ(*d*,*p*)	QZ(2*d*,2*p*)	QZ(2*d*1*f*,2*p*1*d*)	[13*s*8*p*6*d*4*f*,8*s*6*p*4*d*]
ΔE_e[UHF]	47.46	46.18	44.41	44.70
δ[MP2]	−15.74	−16.08	−18.27	−18.30
δ[MP3]	+5.02	+6.02	+5.66	[+5.66]
(δ[MP4],δ[CCSD])	(−1.00,+0.15)	(−1.89,+0.54)	(−2.21,+0.61)	[+0.61]
(δ[MP5],δ[CCSD(T)])	(−1.67,−3.43)	(na,−3.96)	(na,−4.14)	[−4.14]
ΔE_e(corr)	(34.07,33.46)	(na,32.70)	(na,28.27)	[28.53]

$\Delta E_0(5)=\Delta E_e[\mathrm{fp}]+\mathrm{BAC}+\Delta[\mathrm{ZPVE}]=28.5-2.7-1.6=24.2$ kcal mol^{-1}

$\Delta H^\circ_{f,0}(\mathrm{NCO};5)=\Delta E_0(5)-\Delta H^\circ_{f,0}(\mathrm{H})+\Delta H^\circ_{f,0}(\mathrm{NH})+\Delta H^\circ_{f,0}(\mathrm{CO})$

$=24.2-51.63+86.50-27.20=+\mathbf{31.9}$ kcal mol^{-1}

[a] All entries in kcal mol^{-1}; na=not available. See footnote a of Table V.

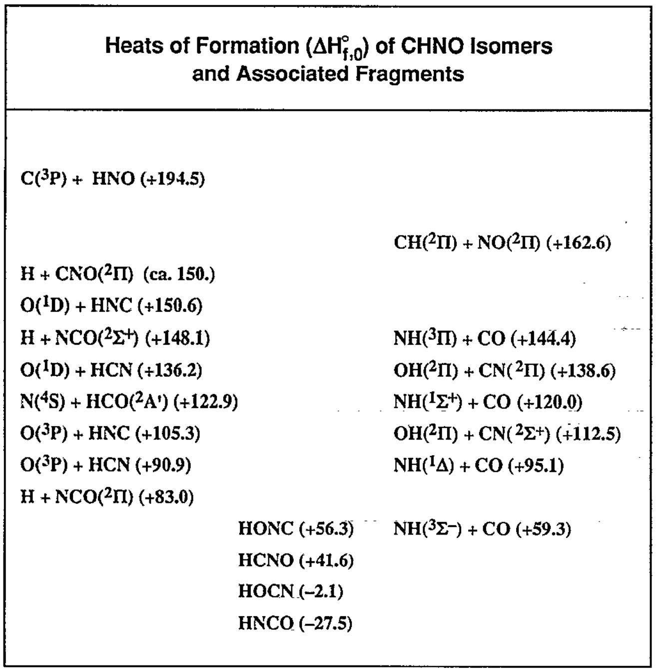

FIG. 1. Thermochemical data for CHNO species. The tabulation is an update of Fig. 5 of Ref. 35 based on the thermochemical revisions ascertained here (n.b., the electronic state of CN appearing in the previous figure should be $^2\Sigma^+$ rather than $^2\Pi$). The assumed heats of formation for the ground electronic states of H, N, O, CO, OH, NH, HCN, HNCO, and NCO were selected from Table III above. Additional $\Delta H^\circ_{f,0}$ values for C, CH, NO, HCO, and HNO were taken from Ref. 26, while that for CN was adopted from Ref. 110. Relative energies for the tetraatomic molecules were extracted from Ref. 35 and anchored to the revised heat of formation of HNCO. Likewise, the $\Delta H^\circ_{f,0}$ values for HNC and $CNO(^2\Pi)$ were, respectively, determined from the (HCN, HNC) (Refs. 111 and 112) and $[NCO(^2\Pi), CNO(^2\Pi)]$ (Ref. 113) isomerization energies. The relative energies for excited-state species were computed from established T_0 values for $O(^1D)$ (Ref. 42), $NH(^1\Delta, ^1\Sigma^+, ^3\Pi)$ and $CN(^2\Pi)$ (Ref. 38), and $NCO(^2\Sigma^+)$ (Ref. 7).

SUMMARY

In the current *ab initio* study, a concerted effort has been made to firmly establish the heat of formation of the cyanato radical. Additional reference points were first added to the available thermochemical data base by determining the refined values $\Delta H^\circ_{f,0}(\text{HNCO}) = -27.5(5)$ kcal mol^{-1} and $\Delta H^\circ_{f,0}(\text{HCN}) = 31.9(5)$ kcal mol^{-1} by means of high-level theoretical predictions for well-behaved isogyric reactions. Subsequently, five independent routes to $\Delta H^\circ_{f,0}(\text{NCO})$ were pursued [Methods (1)–(5)]. In Methods (1) and (2), D_0(H–NCO) and the proton affinity of NCO$^-$ were respectively evaluated by theoretical means, whence two values of $\Delta H^\circ_{f,0}(\text{NCO})$ were ascertained from the heat of formation of HNCO, as well as precise empirical values for EA(NCO) and IP(H) in the latter case. In Method (3) a direct theoretical probe of D_0(N–CO) was used to find $\Delta H^\circ_{f,0}(\text{NCO})$, whereas in Method (4) a transformation involving fragmentation of the C═O bond in the cyanato radical was investigated to arrive at this quantity. Finally, in Method (5) the thermochemistry of the reaction by which a nitrogen atom is transferred from triplet imidogen to carbon monoxide was analyzed to determine $\Delta H^\circ_{f,0}(\text{NCO})$. An extraordinary level of agreement is displayed by the predictions of these five disparate methods, providing the definitive result $\Delta H^\circ_{f,0}(\text{NCO}) = 31.4(5)$ kcal mol^{-1} and resolving widespread confusion among conflicting experimental values for this heat of formation.

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