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The H-NCO bond energy and ΔH_f^0 (NCO) from photoionization mass spectrometric studies of HNCO and NCO

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A photoionization mass spectrometric study of HNCO yields the ionization potential (I.P.) (HNCO) = 11.595 ± 0.005 eV and the appearance potential (A.P.) (NCO⁺/HNCO) $\leq 16.53_2 \pm 0.01_1$ eV at 0 K. A similar study of NCO (generated by F+HNCO) gives I.P. (NCO) = 11.759 ± 0.006 eV. These observations lead to D_0 (H-NCO) $\leq 110.1 \pm 0.3$ kcal/mol. Additional analysis enables one to infer 28.4 ± 0.5 kcal/mol $\leq \Delta H_{f_0}^0$ (NCO) $\leq 32.8 \pm 0.7$ kcal/mol. The implication of these results for kinetic modeling of the processes for reduction of NO_x is discussed.

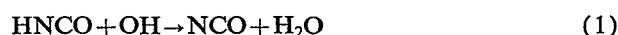
I. INTRODUCTION

Isocyanic acid (HNCO) has a long and illustrious history in the annals of chemistry. Its silver salt was identified in 1823 by Wöhler and, a year later, the empirical formula of the silver salt of fulminic acid (HCNO) was established by Liebig and Gay-Lussac.¹ After some controversy, the appellation "isomer" was first employed to describe these two species having the same empirical formula, but different molecular structures.¹ In 1977, Poppinger, Radom, and Pople² calculated the relative energies of HNCO and HCNO, and also HOCN and HONC. Since 1989, five other *ab initio* calculations^{1,3-6} have been reported on these relative energies. The results are summarized in Table I. Although the calculations have become increasingly more sophisticated, the basic conclusions of Poppinger *et al.* are consistently maintained. The most stable isomer is HNCO, and fulminic acid (HCNO) is less stable by ≥ 3 eV. These two are the only isomers that have been prepared for experimental study in the gas phase, although cyanic acid (HOCN) is predicted² to be isolable and only ~ 1 eV less stable than HNCO. To our knowledge, no experimental data exist on the stability of the three higher energy isomers. (Hop *et al.* have shown that they are stable on a microsecond time scale by neutralization reionization mass spectrometry.⁷) Even the heat of formation of the most stable isomer HNCO has been in dispute. Recently, Spiglanin *et al.*⁸ reviewed prior results and obtained the current best value $\Delta H_{f_{298}}^0$ (HNCO) = $-24.9^{+0.7}_{-2.8}$ kcal/mol.

The magnitude of the H-NCO bond energy [D (H-NCO)] is, of course, intimately related to ΔH_f^0 (NCO). This latter quantity has, until recently, been thought to exceed 36 kcal/mol. Two compendia have listed $\Delta H_{f_{298}}^0$ (NCO) = 37 ± 3 (Ref. 9) and 42 ± 5 kcal/mol,¹⁰ and a more recent inference yielded 36.1 ± 1 kcal/mol.¹¹ In 1992, Cyr *et al.*¹² studied the photodissociation of NCO into N and CO, and deduced $\Delta H_{f_{298}}^0$ (NCO) = 30.5 ± 1 kcal/mol. A primary goal of the present research was to determine D (H-NCO) and ΔH_f^0 (NCO) by an experiment different from those previously used for this purpose, and thereby to establish the relative accuracy of prior results.

Accurate values for D_0 (H-NCO) and ΔH_f^0 (NCO)

are also necessary because of their roles in a potentially important technological process, called RAPRENO_x (rapid reduction of NO_x), for removing oxides of nitrogen from combustion exhausts. Initially proposed by Perry and Siebers,¹³ the process involves injecting cyanuric acid into the exhaust stream. The cyanuric acid sublimates and decomposes into free isocyanic acid HNCO. The isocyanic acid can undergo a complex series of gas phase reactions that result in the elimination of NO. Miller and Bowman¹⁴ have developed a kinetic scheme that includes 105 reactions. The dominant route involves



followed by



N₂O is then decomposed by collision with a third body at sufficiently high temperature, or by reaction with OH to form N₂ + HO₂. It is clearly beyond the scope of this study to probe deeply into the entire reaction scheme. We focus primarily on two points.

(1) In their reaction scheme, Miller and Bowman¹⁴ employ a heat of formation $\Delta H_{f_{298}}^0$ (NCO) = 38.1 kcal/mol, $\Delta H_{f_{298}}^0$ (HNCO) = -24.9 kcal/mol, and hence D_{298} (H-NCO) = 115.1 kcal/mol. Are these values sufficiently accurate for the model? In their modeling of the reaction of O atoms with HNCO, they include two channels



and



but neglect a third



Mertens *et al.*¹⁵ have recently found that reaction (3c) is larger than reaction (3a) above 2120 K and probably at much lower temperatures. Could this result from a lower value for D (H-NCO)?

(2) Miller and Melius¹⁶ have directed their attention to the relative importance of two parallel reactions presumably occurring in the RAPRENO_x process

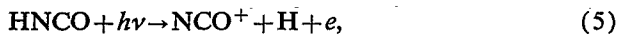
TABLE I. The relative heats of formation of CHNO isomers from *ab initio* calculations (in kilocalories per mole).

HNCO	HOCN	HCNO	HONC	Ref.
0	21.1	79.7	81.3	2
0	21.2	73.6	81.3	1
0	25.4	74.2		3
	25.3	68.1		
0	25.1	68.1	89.1	4
	24.5	68.0	87.9	
0	25.9	69.1	83.7	5
0	25.4	69.1	83.8	6

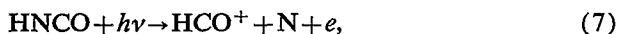


They find better agreement with experiment for reaction (4a) if D_0 (H-NCO) = 112.07 kcal/mol than with 113.67 kcal/mol. We would like to test the validity of either of these values.

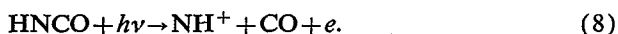
The approach we shall utilize here is photoionization mass spectrometry. Ideally, we would like to know the thermochemical thresholds for the reactions



Subtraction of ΔH [reaction (6)] from ΔH [reaction (5)] would give directly the H-NCO bond energy. Then, if we accept ΔH_f^0 (HNCO) given by Spiglanin *et al.*,⁸ we can immediately determine ΔH_f^0 (NCO). Alternatively, we can in principle determine our own value for ΔH_f^0 (HNCO) by studying other fragmentation onsets, e.g.,



or



However, as we shall see, there are problems with determining accurate thermochemical thresholds for reactions (7) and (8). Reaction (7), which is thermochemically the lowest energy process for fragmentation, requires rearrangement and a change in multiplicity, as HNCO^+ is most likely formed as a doublet, whereas $\text{HCO}^+ (^1\Sigma) + \text{N} (^4S)$ correlate to a quartet surface. Prior evidence^{17,18} shows that HCO^+ is formed with excess kinetic energy, and hence a useful thermochemical threshold cannot be anticipated. Reaction (8) occurs at much higher energy, where a "kinetic shift" of the threshold to still higher energy must be expected.

In Table II, we list some calculated ionization and appearance potentials for HNCO, based on currently available thermochemical data, together with older electron impact measurements.^{17,18} Several features in this table are noteworthy.

(1) Although Bogan and Hand¹⁸ calibrated their determination of I.P. (HNCO) against a standard, their ionization potential for the parent ion is still ~ 0.5 eV higher than the value obtained by photoelectron spectroscopy. If

TABLE II. Ionization and appearance potentials from HNCO, from available thermochemical data, and earlier electron impact experiments.

Ion	Thermochemical ^a	Appearance energy (eV)	
		Electron impact	
		Bogan and Hand ^b	Rowland <i>et al.</i> ^c
HNCO^+	$(11.60 \pm 0.01)^d$	12.15 ± 0.05	$(11.60 \pm 0.01)^d$
HCO^+	14.50 ^e	15.76	15.1–15.3
NCO^+	16.61 ^f	16.66	< 16.1
	16.37 ^g		
NH^+	17.06 ^h	17.26	< 17.7
NO^+	17.41 ⁱ	15.76	...
HNC^+	18.19 ^j		
H^+	18.21		
	18.45		
HCN^+	18.58 ^k		
O^+	18.60		
OH^+	19.00 ^l		
CN^+	20.01 ^m		

^aSpiglanin *et al.* (Ref. 7) have given $\Delta H_{f,298}^0$ (HNCO) = $-24.9^{+0.7}_{-2.8}$ kcal/mol, which is equivalent to $\Delta H_{f,0}^0$ (HNCO) = $-24.2^{+0.7}_{-2.8}$ kcal/mol. Auxiliary thermochemical data are from Ref. 10 when not otherwise stated.

^bReference 18.

^cReference 17.

^dReference 21.

^eUsing ΔH_f^0 (HCO) = 9.9 ± 0.2 kcal/mol (Ref. 10) and I.P. (HCO) = 8.14 eV [from J. M. Dyke, J. Chem. Soc. Faraday Trans. **83**, 69 (1987)].

^fUsing ΔH_f^0 (NCO) = 36.0 kcal/mol (Ref. 11) and I.P. (NCO) = 11.76 eV (Ref. 19).

^gUsing ΔH_f^0 (NCO) = 30.4 kcal/mol (Ref. 12) and I.P. (NCO) = 11.76 eV (Ref. 19).

^h ΔH_f^0 (NH⁺) = 396.3 ± 0.3 kcal/mol from Ref. 33.

ⁱUsing I.P. (NO) = 9.26 eV from K. Muller-Dethlefs, M. Sander, and E. W. Schlag, Chem. Phys. Lett. **112**, 291 (1984).

^jUsing ΔH_f^0 (HNC) = 48 ± 2 kcal/mol and I.P. (HNC) = 12.5 ± 0.1 eV given by Ref. 9.

^kUsing I.P. (HCN) = 13.60 ± 0.01 eV from J. Kreile, A. Schweig, and W. Thiel, Chem. Phys. Lett. **87**, 473 (1982).

^lUsing I.P. (OH) = 13.0170 ± 0.002 eV from R. T. Wiedmann, R. G. Tonkyn, and M. S. White, J. Chem. Phys. **97**, 768 (1992).

^mUsing I.P. (CN) = 14.03 ± 0.02 eV from J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).

we thereupon reduce their reported appearance potential (A.P.) (HCO^+) and A.P. (NCO^+) by ~ 0.5 eV, the resulting values are rather close to those reported by Rowland *et al.*¹⁷

(2) The value of A.P. (NH⁺) reported by Bogan and Hand seems to be ~ 0.5 eV lower than that of Rowland *et al.* without any reduction. It is also rather close to the thermochemical value. Their A.P. (NO⁺) is about 1.7 eV lower than the thermochemical value.

(3) For HCO^+ , the appearance potential given by Rowland *et al.*, and the reduced value of Bogan and Hand, are both about 0.7–0.8 eV higher than the thermochemical value. This observation is consistent with the inference that rearrangement and a change in multiplicity give rise to a barrier for this decomposition, resulting in excess kinetic energy for the product and a delayed onset.

(4) The A.P. (NCO^+) of Bogan and Hand is rather close to the thermochemically deduced values. That of

Rowland *et al.* is significantly lower, implying ΔH_f^0 (NCO) < 24.3 kcal/mol which is well below the lowest value proposed for ΔH_f^0 (NCO) (30.5 kcal/mol).

In summary, the electron impact measurements provide a qualitative indication of the dissociative ionization thresholds from HNCO, but they are quantitatively unreliable. The reported appearance potentials are sometimes larger than the thermochemically anticipated values, which is often observed in electron impact measurements, but also sometimes below the thermochemically calculated onsets, which is more questionable.

The appearance potential of NCO^+ from HNCO depends on three quantities that may require further study (a) the heat of formation of HNCO, for which Spiglanin *et al.*⁸ appear to have a fairly reliable value; (b) the heat of formation of NCO; and (c) the ionization potential of NCO. Dyke *et al.*¹⁹ obtained a photoelectron spectrum of NCO, following the reaction of F atoms with HNCO. Their photoelectron spectrum in the threshold region was a superposition of bands from HNCO and NCO. To arrive at the adiabatic I.P. of NCO (11.76 ± 0.01 eV), it was necessary for them to subtract the HNCO contribution. One of the goals of the present research was to determine the adiabatic ionization potential of NCO by photoionization mass spectrometry, where superposition from HNCO is excluded.

II. EXPERIMENTAL ARRANGEMENT

The basic apparatus consisting of a tunable vacuum ultraviolet (VUV) light source, an ionization region, and a mass spectrometer to identify the ions of interest has been described previously.²⁰ The bandwidth of the VUV monochromator for these experiments was 0.84 \AA [full width at half-maximum (FWHM)]. Isocyanic acid was prepared by dropwise addition of a concentrated aqueous solution of potassium cyanate to phosphoric acid. The evolved HNCO was driven out by a steady stream of nitrogen, collected in a dry ice-acetone trap, and subsequently introduced into the apparatus. The NCO species was prepared *in situ* by the reaction of F atoms (generated in a microwave discharge through F_2) with HNCO.

III. EXPERIMENTAL RESULTS

A. Photoionization of HNCO

1. Overview

The mass spectrum of HNCO observed at $584 \text{ \AA} \equiv 21.2$ eV is listed in Table III. These relative intensities must be considered qualitative, as no correction was applied for the mass discrimination of the quadrupole mass spectrometer, nor for discrimination due to fragment kinetic energies. Nonetheless, it bears a qualitative resemblance to earlier electron impact mass spectra obtained with 70 eV electrons.^{17,18} The parent ion is clearly the most intense, followed by NCO^+ , HCO^+ , and NH^+ . All other peaks are <10% of HNCO^+ in the electron impact spectra, and <1% in Table III, except for NO^+ (1.3%). On this basis, which is consistent with the expected intensities based on

TABLE III. Photoionization mass spectrum of HNCO at $584 \text{ \AA} \approx 21.2$ eV.

<i>m/e</i>	Species	Relative intensity
43	HNCO^+	100.0
42	NCO^+	56.1
31	HNO^+	<0.1
30	NO^+	1.2
29	HCO^+	22.1
27	HCN^+	<0.9
26	CN^+	0.05
15	NH^+	13.1
14	N^+	0.0 ₅
13	CH^+	<0.0 ₁

appearance potentials given in Table II, we have concentrated our efforts on the four major ions HNCO^+ , NCO^+ , HCO^+ , and NH^+ .

An overview of the photoion yield curves of these species is displayed in Fig. 1. The relative intensities are meaningful here, when the qualifying statements (*vide supra*) are taken into account. As expected, the HNCO^+ intensity dominates throughout the region from the ionization potential to 640 \AA . Some autoionizing structure can be seen in the parent ion and is discussed below. The order of appearance of the fragments is $\text{HCO}^+ < \text{NCO}^+ < \text{NH}^+$, in accord with the expectations of Table II.

2. HNCO^+

The overview in Fig. 1 reveals two regions of relatively sharp autoionization structure for HNCO^+ : (1) between ~ 1000 – 1070 \AA and (2) between ~ 800 – 900 \AA . We shall therefore find it convenient to discuss this spectrum in two segments. In Fig. 2, an expanded view of the region between 1000 – 1080 \AA is shown. The onset of ionization is relatively abrupt. The half-rise point, which we choose as the adiabatic I.P. is $1069.3 \pm 0.5 \text{ \AA} \equiv 11.595 \pm 0.005$ eV. This value is in excellent agreement with Eland's²¹ photoelectron spectroscopic result 11.60 ± 0.01 eV, but slightly lower than the photoelectron spectroscopic (PES) value of Cradock *et al.*²² 11.62 ± 0.02 eV.

The peak shapes here are irregular. They have an average spacing of about 550 cm^{-1} . The prominent peak wavelengths are listed in Table IV. In the second photoelectron band, Eland²¹ observes a mean vibrational frequency of 565 cm^{-1} , with "a distinct increase in spacing towards higher vibration quantum numbers." Cradock *et al.*²² report a "progression in 610 cm^{-1} ." Both Eland and Cradock *et al.* assign this frequency to a NH bend in the cation. We interpret this portion of the photoion yield curve as being due to autoionization from one or more Rydberg states converging to a limit given by the second ionization potential. Eland gives the vertical I.P. for this band as 12.39 ± 0.1 eV (perhaps 0.01 eV was intended), whereas Cradock *et al.* obtain 12.30 ± 0.02 eV. Using Eland's vertical I.P. and the criterion that successive members of a Rydberg series should have an approximately constant quantum defect, we find some support for a decomposition of the spectrum into three Rydberg members,

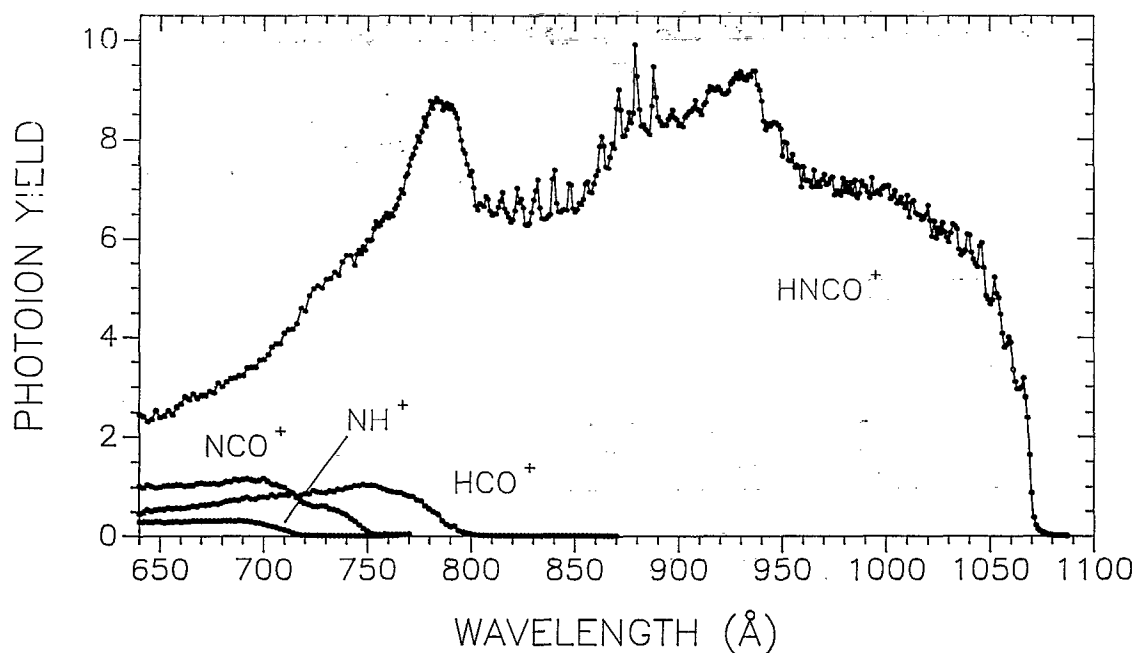


FIG. 1. Photoion yield curves of the major species in the photoionization of HNCO between 640–1090 Å. Wavelength resolution = 0.84 Å (FWHM). The relative intensities shown are the measured ones, subject to mass and kinetic energy discrimination in the quadrupole mass spectrometer.

each with its vibrational manifold. The diagonal line in Fig. 2 connects the vertical excitation energies of the successive Rydberg members. In this interpretation, the vibrational levels of successive Rydberg states partly overlap, thereby accounting for the irregular shapes. The average quantum defect is about 0.5 (mod 1), characteristic of a p -type Rydberg orbital. The qualitative description of the orbital from which the electrons are excited (to Rydberg levels) or ejected (to form the second photoelectron band) has been given by Eland and Cradock *et al.* as the in-plane, nonbonding a' orbital, derived from a π_g -like orbital (as in CO_2) in lower symmetry. Chang,²³ using the HAM/3

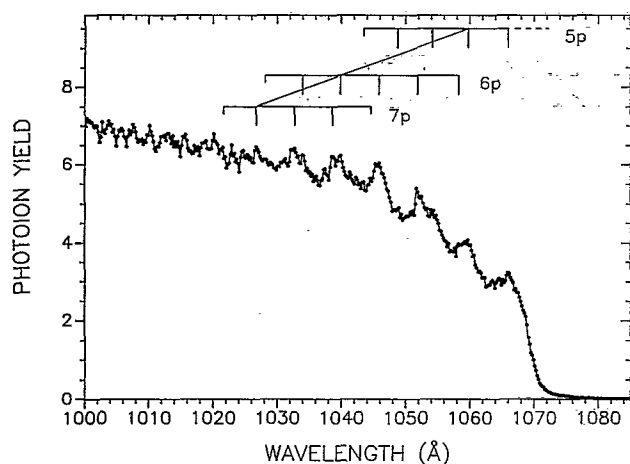


FIG. 2. An expanded view of the photoion yield curve of HNCO^+ (HNCO) between 1000–1080 Å, with suggested assignments for the autoionization peaks.

semiempirical molecular orbital (MO) method, describes this orbital as $9a'$, whereas the uppermost occupied orbital (also derived from π_g) is $2a''$, and hence the out-of-plane component. In a simplistic view, a π_g molecular orbital has a symmetry resembling a d -like atomic orbital. Hence, excitation from such an orbital into p -like Rydberg levels is plausible. The tentative assignment of the various peaks into components of Rydberg levels is presented in Table IV.

The photoion yield curve of HNCO^+ (HNCO) between 750–950 Å appears in Fig. 3. The autoionization structure is now sharper and more prominent. The average spacing is about 1100 cm^{-1} . The peak positions and their assignments are listed in Table V. Eland observes a mean vibrational spacing of 1113 cm^{-1} in the third photoelectron band, whereas Cradock *et al.* report a progression in 1120 cm^{-1} . This frequency presumably corresponds to the symmetric stretch of the NCO skeleton. Eland gives $15.54 \pm 0.05 \text{ eV}$ as the adiabatic I.P. for this band, whereas Cradock *et al.* find $15.8 \pm 0.1 \text{ eV}$ for the vertical I.P. Our analysis assumes that the autoionization features can be ascribed to Rydberg states converging on the I.P. of the third photoelectron band. By shifting the adiabatic I.P. from $15.54 \pm 0.05 \text{ eV}$ to 15.49 eV , it is possible to identify three consecutive members of a Rydberg series, with an almost constant quantum defect δ of -0.02 (mod 1) , and a fourth Rydberg member with $\delta = +0.03 \text{ (mod 1)}$. The Franck-Condon envelope in each Rydberg member is consistent with that in the third photoelectron band. We tentatively assign the Rydberg members with $\delta = -0.02$ to a d -like series, and the single member with $\delta = +0.03$ to an s -like Rydberg.

The current view^{23,24} is that this third band really con-

TABLE IV. Prominent autoionization features of HNCO in the region ~ 1000 – 1070 Å and their tentative assignment.

Assignment	λ (Å) ^a	E (eV) ^b	n^*						
			I.P. (eV) = ^c						
			12.18	12.25	12.32	12.39	12.46	12.53	12.60
5p	1065.9	11.632			4.44 ₇				
	1059.7	11.700				4.44 ₀			
	1054.1	11.762					4.41 ₅		
	1048.7	11.823						4.38 ₆	
	(1043.5)	(11.882)							4.35 ₂
6p	1058.3	11.715	5.41 ₂						
	1051.9	11.787		5.41 ₉					
	1045.9	11.854			5.40 ₅				
	1039.9	11.923				5.39 ₆			
	1034.0	11.991					5.38 ₅		
	(1028.0)	(17.061)						5.38 ₅	
7p	(1044.5)	(11.870)	6.62 ₇						
	1038.6	11.938		6.60 ₀					
	1032.7	12.006			6.58 ₁				
	1026.7	12.076				6.58 ₃			
	(1021.3)	(12.140)					6.51 ₉		

^a ± 0.5 Å.^b ± 0.005 eV.^cFrom Ref. 21 based on the vertical I.P. = 12.39 eV and average spacing of 565 cm^{-1} for the second PES band.

sists of two bands, split very slightly (only 0.02 eV, according to Chang²³). They would correspond to the π_u orbital of CO₂. From an atomic perspective, this orbital has p -like symmetry. Hence, excitation to d -like or s -like Rydberg levels may be expected and tends to support the assignments of the Rydberg features observed.

In Fig. 3, one can see a broad band between ~ 750 – 800 Å, with some weak indication of fine structure, estimated to have spacings of $430 \pm 100\text{ cm}^{-1}$. It is similar in appearance to the fourth photoelectron band in Eland's spectrum. He notes²¹ that it "is almost continuous, but part of a long progression in 450 cm^{-1} can be distinguished at high res-

olution." Cradock *et al.*²² note a progression in 460 cm^{-1} for this band, for which they give $17.50 \pm 0.02\text{ eV}$ as the vertical I.P. Unfortunately, there is an obvious typographical error in Eland's paper, but his figure is consistent with

TABLE V. Autoionization features of HNCO in the region ~ 800 – 900 Å and their tentative assignment.

Assignment	λ (Å) ^a	E (eV) ^b	n^*	
			I.P. (eV) =	
			15.49 ^c	15.54 ^d
3d, $v'=0$	888.0	13.962	2.98 ₄	2.93 ₇
$v'=1$	879.2	14.102		
$v'=2$	870.6	14.241		
$v'=3$	862.8	14.370		
$v'=4$	855.4	14.494		
4d, $v'=0$	847.6	14.628	3.97 ₂	3.86 ₂
$v'=1$	839.6	14.767		
$v'=2$	831.7	14.907		
$v'=3$	824.0	15.047		
$v'=4$	(817.0)	(15.176)		
5d, $v'=0$	829.8	14.941	4.98 ₀	4.76 ₈
$v'=1$	822.0	15.083		
$v'=2$	814.6	15.220		
$v'=3$	807.4	15.356		
$v'=4$	(800.0)	(15.498)		
4s, $v'=0$	885.0	14.010	3.03 ₂	2.98 ₂
$v'=1$	876.3	14.149		
$v'=2$	867.9	14.286		
$v'=3$	859.7	14.422		
$v'=4$	(852.0)	(14.552)		

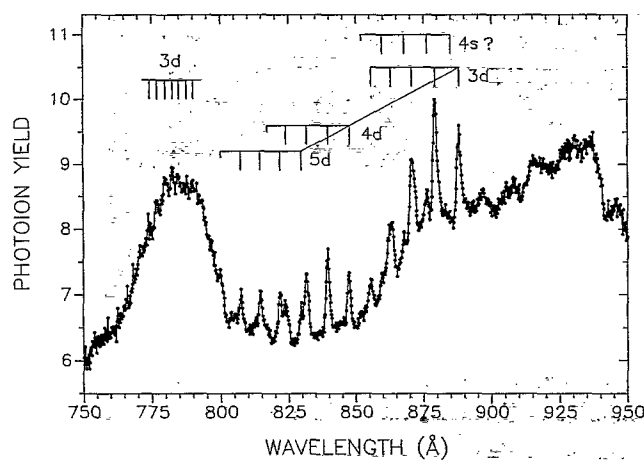
^a ± 0.5 Å.^b ± 0.008 eV.^cFitted adiabatic I.P. from $nd, v'=0$, $n=3$ – 5 , Rydberg members.^dAdiabatic I.P. of the third PES band from Ref. 21.

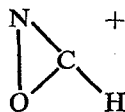
FIG. 3. An expanded view of the photoion yield curve of HNCO⁺ (HNCO) between 750–950 Å, with suggested assignments for the autoionization peaks.

a value of ~ 17.5 eV. The broad band in the photoion yield curve is most likely the first Rydberg member of a series converging to an I.P. corresponding to that of the fourth photoelectron band. With a band maximum at ~ 783 Å, the Rydberg formula gives $n^* \sim 2.86$, or $\delta \approx -0.14$ (mod 1). This is probably a $3d$ -like orbital, but could conceivably be $4s$. The excitation arises from a $7a'$ orbital, according to Chang,²³ and it presumably corresponds to a σ_u orbital in CO_2 . This orbital also has a p -like symmetry viewed as an atomic orbital, and hence excitation to d -like or s -like Rydberg levels is expected.

3. HCO^+

The photoion yield curve of HCO^+ (HNCO) seen in Fig. 1 approaches the background level at ~ 800 Å $\equiv 15.50$ eV, which is 1.0 eV above the thermochemical threshold. The shape of the curve near threshold does not conform well to either a linear or exponential kernel function, convoluted with a Boltzmann thermal function.²⁵ The best fit yields a 0 K threshold of 15.59 ± 0.04 eV. The first departure from threshold occurs at 806 ± 2 Å $\equiv 15.38 \pm 0.04$ eV.

Clearly, some rearrangement is necessary to generate HCO^+ from HNCO^+ . Bogan and Hand¹⁸ performed intermediate neglect of differential overlap (INDO) calculations that showed that a doublet cyclic structure,



was the most stable form of the cation and argued that formation of HCO^+ proceeded through this entity. Recently, Maclagan²⁶ has performed calculations at the second-order Møller-Plesset (MP2)/6-31G* level and concluded that this cyclic structure occurs 2.29 eV above the ground state of the cation. This would still place it at an absolute energy of 13.89 eV, or about 0.6 eV below the thermochemical onset of HCO^+ . The quartet cyclic structure, which Bogan and Hand place at higher energy than the doublet, might be more relevant, as decomposition of such a state would not violate spin conservation rules. Access to this state could conceivably be facilitated by autoionization.

4. NCO^+

An expanded section of the photoion yield curve of NCO^+ (HNCO) is shown in Fig. 4. The curve has been fitted by a linear kernel function, convoluted with a Boltzmann function of the form $Ee^{-E/kT}$, which implies four rotational degrees of freedom.²⁵ HNCO has three rotational degrees of freedom; together with its vibrational heat content, the total internal energy amounts to 0.0494 eV, whereas four rotational degrees of freedom ($2kT$) is 0.0514 eV. Therefore, the shape of the Boltzmann function should be well approximated by $Ee^{-E/kT}$. Prior to fitting, 0.5% of the HNCO⁺ photoion yield curve was subtracted from the NCO⁺ curve, to take into account the incomplete mass separation between $m/e=43$ (HNCO⁺) and $m/e=42$ (NCO⁺). The magnitude of this mass leakage had

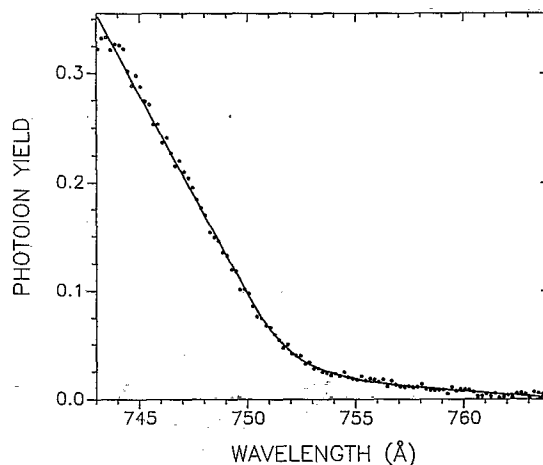


FIG. 4. An expanded view of the threshold region of the photoion yield curve of NCO^+ (HNCO). The curve has been fitted by a linear kernel function convoluted with a Boltzmann function of the form $Ee^{-E/kT}$ (see the text). Prior to fitting, 0.5% of the HNCO⁺ photoion yield curve was subtracted from the NCO⁺ curve to take into account incomplete mass separation between $m/e=43$ (HNCO⁺) and $m/e=42$ (NCO⁺).

been established independently. The best fit between the convolution function and the experimental data yields $16.53_2 \pm 0.01_1$ eV as the 0 K threshold.

5. NH^+

The expanded threshold region for formation of NH^+ (HNCO) is displayed in Fig. 5. The curve has been fitted, as in Sec. III A 4 (*vide supra*) with a function that is a convolution of a linear kernel function and a Boltzmann function $Ee^{-E/kT}$. No background subtraction was required here. The fit is seen to be quite good. It yields an appearance potential of $17.30_7 \pm 0.01_2$ eV at 0 K.

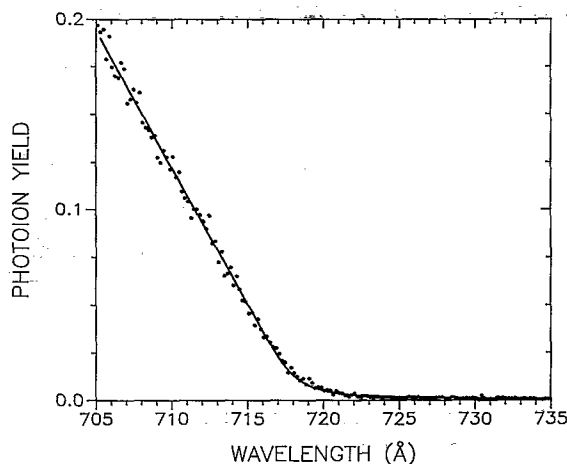
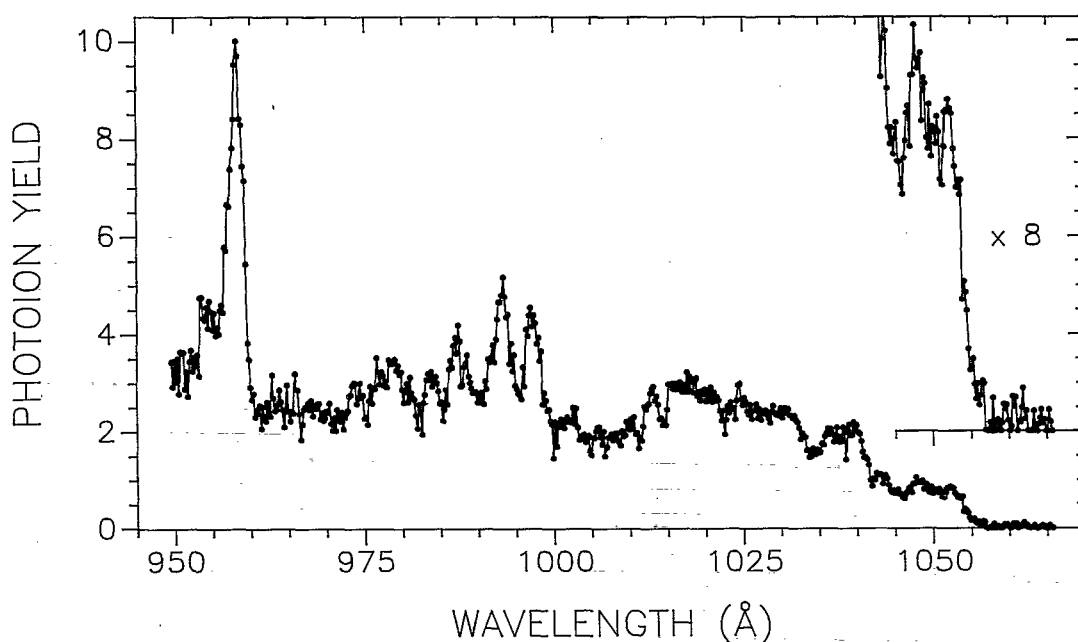


FIG. 5. An expanded view of the threshold region of the photoion yield curve for NH^+ (HNCO). The curve has been fitted with a linear kernel function convoluted with a Boltzmann function of the form $Ee^{-E/kT}$ (see the text).

FIG. 6. Photoion yield curve of NCO^+ (NCO).

B. Photoionization of NCO

The photoion yield curve of $m/e=42$ observed upon reacting HNCO with F atoms is displayed in Fig. 6. The very low background above 1050 Å, together with the observation that $m/e=43$ was substantially reduced during the reaction, is strong evidence for negligible mass leakage from $m/e=43$ to 42. Hence, the curve in Fig. 6 can safely be assigned to NCO^+ (NCO).

The He I photoelectron spectrum of NCO has been measured by Dyke *et al.*¹⁹ They assign four bands in the energy region <15 eV and additional structure at ~18.8 eV. Because our spectrum terminates at 950 Å \equiv 13.05 eV, we shall confine our attention to the first four bands. The first band is reported by Dyke *et al.* to have an adiabatic I.P. of 11.76 ± 0.01 eV, and has higher vibrational components with a mean separation of 1000 ± 30 cm^{-1} . The band is overlaid in part by HNCO (on the low-energy side) and by O_2 (on the high-energy side). The present spectrum (Fig. 6) has a step-like feature near threshold, with some autoionizing structure superposed. We choose the half-rise point of that first step as the adiabatic ionization potential of NCO. It occurs at 1054.4 ± 0.5 Å \equiv 11.759 ± 0.006 eV. Hence, this result confirms the value extracted by Dyke *et al.* from their spectra.

Between ~1050–1015 Å, the photoion yield curve appears to display step-like features with autoionizing structure superposed. The step-like features could represent the higher vibrational levels of the ionic ground state (NCO^+ , $X^3\Sigma^-$). Between ~970–1000 Å, several autoionizing peaks are clearly visible. Their wavelengths and energies are given in Table VI. They do not fit into a simple vibrational progression. Their energies imply that they may be Rydberg members converging to one or both of the next

higher electronic states $a^1\Delta$ (I.P.=12.92 eV) or $b^1\Sigma^+$ (I.P.=13.56 eV). The photoelectron spectrum of Dyke *et al.* reveals that both states display vibrational spacings of ~ 1100 cm^{-1} , ≈ 0.136 eV, but $a^1\Delta$ has a longer progression. We may anticipate that Rydberg states would manifest vibrational progressions similar to that of their convergent ion. Thus, we note in Table VI that the peaks at 996.9 and 987.2 Å are separated by 0.122 eV (985 cm^{-1}) and those at 993.3 and 983.7 Å also by 0.122 eV. The next higher members of these vibrational progressions would be predicted to occur at ~977.7 and ~974.3 Å, and there is some evidence for peaks close to these wavelengths. However, the region around 977–979 Å appears to manifest a blend with additional structure, suggesting still another Rydberg member or Rydberg series.

TABLE VI. Autoionization features in the photoionization spectrum of NCO in the region ~970–1000 Å.

λ (Å) ^a	E (eV) ^b
996.9	12.437
993.3	12.482
991.9 sh ^c	12.500
988.5	12.543
987.2	12.559
983.7	12.604
980.7	12.642
978.7	12.668
976.8	12.693
975.6 sh ^c	12.709
974.1 d ^c	12.728

^a ± 0.5 Å.^b ± 0.006 eV.^csh—shoulder; d—doublet?

We tentatively associate the two vibrational progressions with Rydberg states of two series converging to $a^1\Delta$. Then, assigning the 996.9 and 993.3 Å features as the $v'=0$ members of the respective series, we infer $n^*=5.307$ and 5.573, respectively, from the Rydberg formula. The next higher members, corresponding to $n^*=6.307$ and 6.573, should then occur at 985.7 and 983.6 Å. The latter wavelength corresponds very closely to one of the observed peaks. In fact, it has already been tentatively assigned to $v'=1$ of the preceding Rydberg member. However, the predicted 985.7 Å feature corresponds to a valley. Consequently, this simple analysis is inadequate. It does suggest, however, that overlapping series with the indicated effective quantum numbers can exist in the wavelength region between ~ 975 – 997 Å. We do not rule out the possibility of additional series converging to $b^1\Sigma^+$. However, in addition to the extent of the vibrational progression, a further argument favoring series converging to $a^1\Delta$ is the larger number of allowed Rydberg series one can construct with a $^1\Delta$ core.

The largest peak in the spectrum occurs at 958.1 Å $\equiv 12.941$ eV. Its strong 0–0 transition, and its energy, suggests that it be associated with the fourth band in the photoelectron spectrum of Dyke *et al.* The latter manifests a strong 0–0 peak at 14.73 eV and a very weak 0–1 peak. It has been assigned to formation of NCO^+ , $^3\Pi$, and derives from ionization of an inner 7σ electron, whereas the three lower energy peaks involve ejection from the uppermost 2π orbital. The effective quantum number for the 958.1 Å feature is then $n^*=2.757$, implying that it is the first member of that particular series. The corresponding orbital, from which electron ejection occurs in HNCO (see Sec. III A 2) is labeled $7a'$, and it gives rise to the broad, intense feature in Fig. 3 centered at ~ 783 Å. Its breadth in HNCO has been attributed²¹ to a progression in the N–H bend, which is, of course, absent in NCO. The effective quantum numbers in the two cases 2.76 and 2.86 are fairly close. Hence, the argument given previously for assigning the Rydberg to $3d$ (conceivably $4s$) can be carried over to the present case.

IV. INTERPRETATION OF RESULTS

A. D_0 (H–NCO)

A direct consequence of the present measurements is an upper limit to D_0 (H–NCO). Thus, from A.P. (NCO^+/HNCO) = $16.53_2 \pm 0.01_1$ eV and I.P. (NCO) = 11.759 ± 0.006 eV, we deduce D_0 (H–NCO) $\leq 4.77_3 \pm 0.01_3$ eV $\equiv 110.1 \pm 0.3$ kcal/mol. A lower limit can be inferred by assuming that the kinetic shift that may be influencing A.P. (NCO^+) is less than or equal to the kinetic shift in the higher energy process yielding A.P. (NH^+), as discussed below. This lower limit is D_0 (H–NCO) $> 105.6 \pm 0.5$ kcal/mol.

Prior experimental values are based on the photodissociative threshold for formation of NCO ($\tilde{A}^2\Sigma^+$) from HNCO and on the gas phase acidity of HNCO. Okabe²⁷ found the threshold for $\tilde{A}^2\Sigma^+$ to occur at 1605 ± 2 Å $\equiv 7.725 \pm 0.010$ eV. More recently, Uno *et al.*²⁸ obtained

$1620 \text{ Å} \equiv 7.65_3$ eV for this onset, with no error bar given. The $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi_{3/2}$ excitation energy has been reported²⁹ to be $22\,754.020 \text{ cm}^{-1} \equiv 2.821$ eV for the (000)–(000) transition. Thus, from Okabe, one deduces D (H–NCO) $\leq 4.90 \pm 0.01$ eV $\equiv 113.1 \pm 0.2$ kcal/mol, and from Uno *et al.* D (H–NCO) ≤ 4.83 eV $\equiv 111.4$ kcal/mol. Both of these results were obtained with room temperature HNCO, and hence it is plausible to apply a correction for the internal energy of HNCO, as is done conventionally in the correction of photodissociative ionization thresholds. With this correction, D_0 (H–NCO) $\leq 114.2 \pm 0.2$ kcal/mol (Okabe) and ≤ 112.6 kcal/mol (Uno *et al.*). These upper limits, though consistent with the present results, are significantly higher.

Wight and Beauchamp³⁰ measured the gas phase acidity of HNCO to be 344.7 ± 2 kcal/mol. The gas phase acidity is defined as the enthalpy for the reaction



at 298 K. Using vibrational frequencies for HNCO from Teles *et al.*,¹ and for NCO^- from Bradforth *et al.*³¹ the enthalpy for reaction (9) at 0 K becomes 343.6 ± 2 kcal/mol. Upon introducing I.P. (H) = 13.5984 eV (Ref. 32) and the recently determined³¹ E.A. (NCO) = 3.609 ± 0.005 eV, we arrive at D_0 (H–NCO) = 113.2 ± 2 kcal/mol, which is larger than our upper limit.

The value $\Delta H_{f_0}^0$ (NCO) = 30.4 ± 1 kcal/mol recently obtained by Cyr *et al.*¹² when combined with $\Delta H_{f_0}^0$ (HNCO) = -25.6 ± 0.6 kcal/mol (*vide infra*) yields D_0 (H–NCO) = 107.6 ± 1.2 kcal/mol, which falls midway between our upper and lower limits.

Some recent *ab initio* calculations have either arrived at D_0 (H–NCO) directly, or can be related to it. By direct computation of the energy for the reaction



East *et al.*⁵ initially obtained D_e (H–NCO) = 119 ± 2 kcal/mol or (using their zero point energies) D_0 = 112 ± 2 kcal/mol. It was presumably this result that led them to state that “the experimental value D_0 (H–NCO) = 113.0 (2) kcal/mol (of Okabe) is confirmed.” After the experimental results of Cyr *et al.*¹² appeared, East and Allen⁶ refined their calculation for this process and obtained D_0 (H–NCO) = 110.4 kcal/mol.

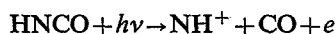
However, East *et al.*⁵ (and later, East and Allen⁶) preferred the results of an alternative calculation, corresponding to reaction (9). This is an isogyric process, which minimizes correlation effects, and does not require “bond additivity corrections.” The initial calculation by East *et al.*,⁵ using an approximate value for the electron affinity (E.A.) of NCO (3.6 ± 0.2 eV) arrived at D_e (H–NCO) = 117.5 ± 4.5 kcal/mol. Thus, the major contribution to their error limit was the uncertainty in E.A. (NCO). By substituting E.A. (NCO) = 3.609 ± 0.005 eV³¹ we infer D_e (H–NCO) = 117.7 kcal/mol, presumably with a much lower error bar, and D_0 (H–NCO) = 110.7 kcal/mol. The later paper by East and Allen⁶ arrives at nearly the same value 110.5 kcal/mol. Thus, the revised calculations of

East and Allen⁶ for both processes are within 0.5 kcal/mol of our upper limit D_0 (H-NCO) $\leq 110.1 \pm 0.3$ kcal/mol.

MacLagan²⁶ has recently calculated the proton affinity of NCO at the G2 level. His value 156.2 kcal/mol refers to reactants and products at 298 K and becomes 155.1 kcal/mol when reduced to 0 K using his frequencies. By introducing I.P. (H) = 13.5984 eV and our current value of I.P. (HNCO) = 11.595 ± 0.005 eV, we obtain D_0 (H-NCO) = 108.9 kcal/mol, which is well within our permissible range.

B. Δ_f^0 (NCO)

The appearance potential observed for reaction (8)



is $17.30_7 \pm 0.01_2$ eV at 0 K. Because $\Delta H_{f_0}^0$ (NH⁺) = 396.3 ± 0.3 kcal/mol (Ref. 33) and $\Delta H_{f_0}^0$ (CO) = -27.20 ± 0.04 kcal/mol (Refs. 9 and 10) are well established, this appearance potential would require $\Delta H_{f_0}^0$ (HNCO) $\cong -30$ kcal/mol, if it were thermochemically significant. Such a value for $\Delta H_{f_0}^0$ (HNCO) is significantly lower than that arrived at by other methods. It would imply that the threshold for NH ($a^1\Delta$) from HNCO observed by Spiglanin and Chandler⁸ should occur at $43\,475\text{ cm}^{-1}$. However, their observed threshold is much lower ($41\,530 \pm 150\text{ cm}^{-1}$). The corresponding value from Okabe's²⁷ results is still lower. Hence, we conclude that A.P. (NH⁺/HNCO) suffers a kinetic shift, or delayed onset. This is not surprising, as it is preceded by two lower energy fragmentation processes (HCO⁺ and NCO⁺).

If we assume that the kinetic shift for NCO⁺ is less than or equal to that for NH⁺ (which is plausible, as both are simple bond cleavages, and NCO⁺ occurs at lower energy), then we can establish a lower limit for $\Delta H_{f_0}^0$ (NCO⁺). Thus,

$$\Delta H_{f_0}^0(\text{NCO}^+) + \Delta H_{f_0}^0(\text{H}) - \text{A.P.}(\text{NCO}^+/\text{HNCO})$$

$$\geq \Delta H_{f_0}^0(\text{NH}^+) + \Delta H_{f_0}^0(\text{CO}) - \text{A.P.}(\text{NH}^+/\text{HNCO}).$$

Introducing A.P. (NCO⁺/HNCO) = $16.53_2 \pm 0.01_1$ eV obtained in Sec. III A 4, and $\Delta H_{f_0}^0$ (H) = 51.633 kcal/mol,¹⁰ we obtain

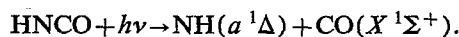
$$\Delta H_{f_0}^0(\text{NCO}^+) \geq 299.6 \pm 0.5 \text{ kcal/mol.}$$

Then, utilizing I.P. (NCO) = 11.759 ± 0.006 eV obtained in this work, we arrive at $\Delta H_{f_0}^0$ (NCO) $\geq 28.4 \pm 0.5$ kcal/mol.

We can also establish an upper limit for $\Delta H_{f_0}^0$ (NCO) from a more precise value of $\Delta H_{f_0}^0$ (HNCO). Two groups have derived this quantity from an indirect determination of the threshold for dissociation into NH and CO. Okabe²⁷ reported thresholds for photodissociation of HNCO into NH($a^1\Delta$) + CO($X^1\Sigma^+$), NH($A^3\Pi$) + CO($X^1\Sigma^+$), NH($c^1\Pi$) + CO($X^1\Sigma^+$), NH($X^3\Sigma^-$) + CO($a^3\Pi$), and NH($A^3\Pi$) + CO($a^3\Pi$). Remarkably, they were all consistent (to ± 0.1 eV) when taking into account the known

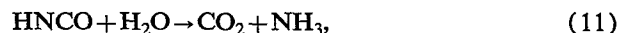
excitation energies of NH and CO. Okabe chose the threshold with the lowest error bar [NH($c^1\Pi$) + CO($X^1\Sigma^+$)], which was 8.79 ± 0.03 eV, together with a $c^1\Pi - X^3\Sigma^-$ excitation energy of 5.41 eV, to arrive at D_0 (HN-CO) $\leq 3.38 \pm 0.1$ eV, or 78 ± 2 kcal/mol. (With a modern value³⁴ of the $c^1\Pi - X^3\Sigma^-$ excitation energy of 5.374 eV, D_0 (HN-CO) would be 78.8 kcal/mol.) He then used ΔH_f^0 (NH) = 81 ± 2 kcal/mol and ΔH_f^0 (CO) = -26.5 ± 0.7 kcal/mol to arrive at ΔH_f^0 (HNCO) = -24 ± 3 kcal/mol, which seemed to be a plausible result. If he had available the current best value³⁵ for $\Delta H_{f_0}^0$ (NH) = 85.5 ± 0.4 kcal/mol and $\Delta H_{f_0}^0$ (CO) = -27.20 ± 0.04 kcal/mol, he would have obtained $\Delta H_{f_0}^0$ (HNCO) = -20 ± 2 kcal/mol. More recently, Uno *et al.*²⁸ have essentially reproduced Okabe's threshold for NH($c^1\Pi$) + CO($X^1\Sigma^+$).

Spiglanin *et al.*⁸ examined the onset for



Their linearly extrapolated onset for this process was $41\,530 \pm 150\text{ cm}^{-1}$, or 5.149 ± 0.019 eV. Upon subtracting the $a^1\Delta - X^3\Sigma^-$ excitation energy³⁴ 1.561 eV, one obtains D (HN-CO) = 3.588 eV $\equiv 82.75 \pm 0.43$ kcal/mol. Upon examining the rotational energy in the NH product, and extrapolating that quantity to zero rotational energy, Spiglanin *et al.*⁸ arrived at "an upper limit to the dissociation energy of $42\,500\text{ cm}^{-1}$," which they incorporated into their error bar. In our interpretation of their data, the excess rotational energy in NH is a consequence of the internal thermal energy of their starting material (HNCO), which has a value of 1.14 kcal/mol at 298 K. Thus, treating their linearly extrapolated threshold for NH ($a^1\Delta$) as we would a linearly extrapolated dissociative ionization threshold, we arrive at D_0 (HN-CO) = $82.75 + 1.14 = 83.89$ kcal/mol. With this value, and the aforementioned $\Delta H_{f_0}^0$ (NH) and $\Delta H_{f_0}^0$ (CO), we obtain $\Delta H_{f_0}^0$ (HNCO) = -25.6 ± 0.6 kcal/mol.

East *et al.*⁵ have recently reported an extensive *ab initio* calculation of this quantity. From their best direct calculation of the energies of HNCO, NH, and CO, they deduce D_e (NH-CO) = 92 ± 2 kcal/mol. Using their zero point energies, we obtain D_0 (HN-CO) = 86.4 ± 2 kcal/mol. Then, employing $\Delta H_{f_0}^0$ (NH) and $\Delta H_{f_0}^0$ (CO), we infer $\Delta H_{f_0}^0$ (HNCO) = -28.1 ± 2 kcal/mol. They also performed an indirect calculation, based on the hypothetical reaction



which is isogyric and involves isoelectronic pairs of reactants and products. From this latter reaction, they obtained $\Delta H_{f_0}^0$ (HNCO) = -26.1 kcal/mol. Both results were (within the respective error bars) in agreement with the inferred experimental value. The latter method, which they preferred, was in particularly good agreement with experiment.

Subsequent to that work, East and Allen⁶ reexamined their calculation of reaction (11). They deduced a lowering of $\Delta H_{f_0}^0$ (HNCO) by 1.4 kcal/mol of which 0.8 kcal/mol

mol was due to an improved basis set and 0.6 kcal/mol due to higher order correlation shifts, resulting in $\Delta H_{f_0}^0$ (HNCO) = -27.5 ± 0.5 kcal/mol. They noted that this result was near the lower limit given by Spiglanin *et al.*⁸ $-24.9_{-2.8}^{+0.7}$ kcal/mol. However, Spiglanin *et al.* offered this latter value as $\Delta H_{f_{298}}^0$ (HNCO). When the correction to 0 K is applied, $\Delta H_{f_0}^0$ (HNCO) = $-24.2_{-2.8}^{+0.7}$ kcal/mol, making the lower limit -27.0 kcal/mol, which barely overlaps with -27.5 ± 0.5 kcal/mol. Spiglanin *et al.* arrived at this lower limit by examining the behavior of the average NH* rotational energies, which they found to increase with increasing photon energy of the dissociation laser "except for the results from the low energy photolysis experiments." Extrapolating this behavior to zero rotational energy, they obtained an upper limit to the dissociation onset of $42\,500\text{ cm}^{-1}$, which is $970\text{ cm}^{-1} \equiv 2.8$ kcal/mol lower than their extrapolated threshold. A more sensitive measure of excess rotational energy in the products might result from the study of CO, which has a much smaller rotational constant ($\sim 1.9\text{ cm}^{-1}$) (Ref. 34) than NH ($\sim 16.5\text{ cm}^{-1}$).³⁴ However, Spiglanin *et al.*⁸ were unable to make such a measurement very near the dissociation threshold due to intense background from the probe laser. We regard their extrapolation of the dissociation onset ($41\,530 \pm 150\text{ cm}^{-1}$) as more definitive than their extrapolation of the rotational energy of NH* to zero ($42\,500\text{ cm}^{-1}$) and, consequently, our inferred value of $\Delta H_{f_0}^0$ (HNCO).

Utilizing $\Delta H_{f_0}^0$ (HNCO) = -25.6 ± 0.6 kcal/mol and A.P. (NCO⁺/HNCO) = $16.53_2 \pm 0.01_1$ eV, we obtain $\Delta H_{f_0}^0$ (NCO⁺) $\leq 304.0 \pm 0.7$ kcal/mol. Subtracting I.P. (NCO) = 11.759 ± 0.006 eV yields $\Delta H_{f_0}^0$ (NCO) $\leq 32.8 \pm 0.7$ kcal/mol. The upper bound implies that there may be some kinetic shift controlling the appearance potential of NCO⁺. The net result of these analyses is

$$28.4 \pm 0.5 \text{ kcal/mol} \leq \Delta H_{f_0}^0 \text{ (NCO)} \\ \leq 32.8 \pm 0.7 \text{ kcal/mol.}$$

Of the various experimental values for this quantity, only the recent one of Cyr *et al.*¹² (30.5 ± 1 kcal/mol) satisfies these limits.

V. SUMMARY AND CONCLUSIONS

(1) From the threshold for photoionization of HNCO⁺ (HNCO), we have determined the adiabatic I.P. of HNCO to be 11.595 ± 0.005 eV, in excellent agreement with an earlier photoelectron spectroscopic value²¹ 11.60 ± 0.01 eV.

(2) The adiabatic ionization potential of NCO⁺ has been measured by photoionization mass spectrometry to be 11.759 ± 0.006 eV, in excellent agreement with another photoelectron spectroscopic result¹⁹ 11.76 ± 0.01 eV.

(3) The appearance potential of NCO⁺ from HNCO was found to be $16.53_2 \pm 0.01_1$ eV at 0 K. As this is an upper limit, combining this value with I.P. (NCO) yields

D_0 (H-NCO) $\leq 4.77_3$ eV $\equiv 110.1 \pm 0.2$ kcal/mol. The corresponding limit for D_{298} (H-NCO) is $\leq 111.8 \pm 0.2$ kcal/mol.

(4) An upper limit $\Delta H_{f_0}^0$ (NCO) $\leq 32.8 \pm 0.7$ kcal/mol can be derived from the upper limit for D_0 (H-NCO), a slightly modified value of $\Delta H_{f_0}^0$ (HNCO), and the assumption of zero kinetic shift in the appearance potential of NCO⁺ (HNCO). A plausible lower limit $\Delta H_{f_0}^0$ (NCO) $\geq 28.5 \pm 0.5$ kcal/mol can be inferred if it is assumed that the kinetic shift for NCO⁺ (HNCO) is as large as the kinetic shift for the higher energy process NH⁺ (HNCO). The recent value of Cyr *et al.*¹² is contained within these limits, but earlier ones are above our upper limit. For $\Delta H_{f_{298}}^0$ (NCO), the above limits are increased by 0.1 kcal/mol.

(5) These results for D_0 (H-NCO) and $\Delta H_{f_0}^0$ (NCO) imply that kinetic modeling studies of the RAPRENOx process, which have used larger values for these quantities, should perhaps be reassessed with revised values.

(6) Autoionization structure is observed in the photoion yield curves of HNCO⁺ (HNCO) and NCO⁺ (NCO). Assignments are made for the observed peaks based on the available He I photoelectron spectra.

ACKNOWLEDGMENT

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