

## The heat of formation of chlorine-isocyanate and the relative stability of isoelectronic molecules: An experimental and theoretical study

Yuanyuan Ji

*Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106*

Petia Bobadova-Parvanova

*Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322*

Chris Larson and Peter C. Samartzis

*Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106*

Keiji Morokuma

*Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322*

Jim Jr-Min Lin, Tao-Tsung Ching, and Chanchal Chaudhuri

*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, Republic of China*

Shih-Huang Lee

*National Synchrotron Radiation Research Center, 101 Hsin-Ann Rd., Science-Based Industrial Park, Hsinchu 30077, Taiwan, Republic of China*

Alec M. Wodtke<sup>a)</sup>

*Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106*

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Accurate thermochemical data of small molecules are invaluable to the progress of every aspect of chemistry, especially in the atmosphere, combustion and industry. In this work, photofragmentation translational spectroscopy and 1st principles electronic structure theory reveal the literature value of the heat of formation of chlorine-isocyanate to be in error by more than 40 kcal/mol. We report a revised experimental value for  $D_0(\text{Cl-NCO})=51\pm 3$  kcal/mol which leads to a  $\Delta H_f(\text{ClNCO})=8.5\pm 3$  kcal/mol. High level *ab initio* (CCSD(T)) electronic structure calculations extrapolated to the complete basis set limit give  $D_0(\text{Cl-NCO})=56.3$  kcal/mol, in good agreement with experiment. In light of the present results, the destabilization of azides relative to isoelectronic isocyanates has been evaluated empirically for three pairs of related molecules. It is found to be 90–110 kcal/mol, and has been attributed mainly to the weakening of the N–NN bond relative to the N–CO bond. Electronic structure calculations employing decomposition analysis suggest that, compared to homopolar  $\text{N}_2$ , the  ${}^{+\delta}\text{CO}^{-\delta}$   $\pi$  polarity provides better orbital interaction (charge transfer) and electrostatic attraction and results in a closer encounter and larger stabilization between the fragments and that this is the origin of isoelectronic destabilization of azides relative to the isocyanates. © 2006 American Institute of Physics. [DOI: 10.1063/1.2210934]

In light of recent experimental<sup>1–3</sup> and theoretical<sup>4</sup> work concerning the possibility of producing cyclic- $\text{N}_3$  from  $\text{X-N}_3$  photolysis, we undertook a study of the collision free photochemistry of the isoelectronic CINCO molecule to explore conditions where the theoretically-predicted cyclic-NCO species might be found.<sup>5–7</sup> The strategy of the study was to measure high resolution translational energy release distributions of products of ultraviolet (UV) photolysis of the N–Cl bond fission reaction (1):



<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: wodtke@chem.ucsb.edu

Through knowledge of accurate thermochemistry, the measurement of the translational energy release can be used to derive the internal energy content of the NCO. Formation of the cyclic isomer of NCO would appear as a second lower energy peak in the translational energy release distribution, with an excitation energy corresponding to the cyclization energy of NCO.

A full exposition of the experimental methods used in this work will appear in a future article. For now we mention only that the methods used were nearly identical to those reportedly recently for experiments on  $\text{ClN}_3$ .<sup>3</sup> Here a molecular beam of CINCO seeded in He was formed in a reactor using  $\text{Cl}_2$  and  $\text{AgNCO}$ .<sup>8</sup> Photolysis was carried out at 193 nm using an ArF laser. The photo-ionizing radiation from the synchrotron was at a photon-energy of

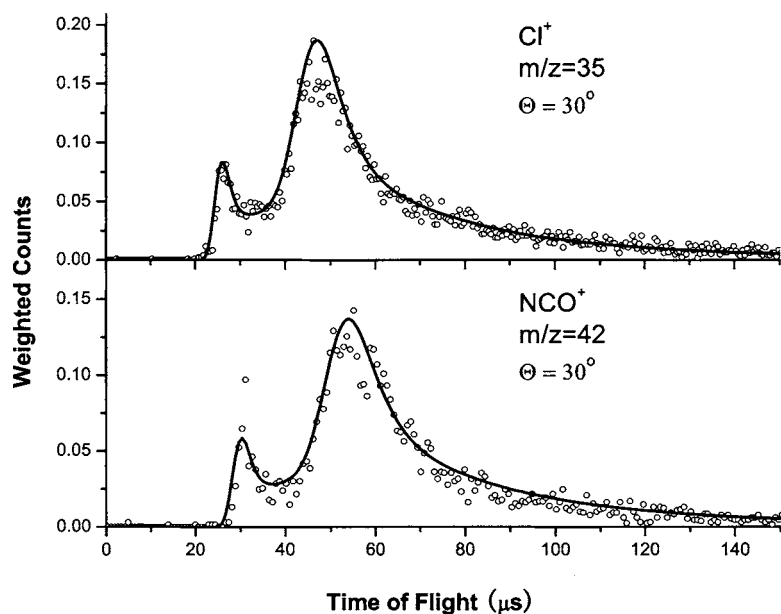


FIG. 1. Representative time-of-flight (TOF) spectra of the major products of the primary collision-free photodissociation of chlorine-isocyanate,  $\text{ClNCO} \rightarrow \text{Cl} + \text{NCO}$ , at 193 nm. The upper and lower traces show the results for detection of  $\text{Cl}^+$  and  $\text{NCO}^+$ , which result from synchrotron non-dissociative ( $h\nu = 14.8$  eV) photoionization of Cl and NCO, respectively. The products are detected at a laboratory-frame recoil angle of  $30^\circ$  with respect to the  $\text{ClNCO}$  molecular beam. The open circles represent the data and the solid lines are the forward convolution simulation of the  $\text{Cl} + \text{NCO}$  forming channel using the center-of-mass frame translational energy distribution,  $P(E_T)$ , shown in Fig. 2. These TOF spectra were taken sequentially to ensure nearly identical experimental conditions. The excellent fit to the data of both Cl and NCO with a single  $P(E_T)$  shows that the two photo-fragments are “momentum-matched,” unambiguously proving they result from reaction (1) and that NCO does not undergo unimolecular dissociation on the  $100 \mu\text{s}$  time-scale of the experiment.

$14.8 \pm 0.2$  eV, well above the ionization threshold of Cl and NCO, but still below the dissociative ionization limits of  $\text{ClNCO}$ , NCO, NCl, or CO. Figure 1 shows neutral time-of-flight (TOF) data obtained with the photofragmentation translational spectroscopy apparatus at the NSRRC in Hsinchu, Taiwan, for one angle of recoil and two values of  $m/z = 35$  ( $\text{Cl}^+$ ) and  $42$  ( $\text{NCO}^+$ ). We also observed extremely weak  $m/z = 49$  ( $\text{NCl}^+$ ) and  $m/z = 28$  ( $\text{CO}^+$ ) signals (which suggests that  $\text{ClNCO} \rightarrow \text{NCl} + \text{CO}$  is a minor channel) and negligible  $m/z = 14$  ( $\text{N}^+$ ) signal. The neutral TOF from the position where ArF laser photolysis is accomplished to the position where vacuum ultraviolet (VUV) photoionization of photo-products occurs (10.05 cm away) is the  $x$ -axis of Fig. 1. The open circles in Fig. 1 are the TOF data-ion counts recorded by a Daly-style ion detector at a specific  $m/z$ -value passed by a quadrupole mass filter. The ion counts have been normalized to number of laser shots, laser power, and  $\text{ClNCO}$  concentration in the molecular beam, as monitored by a residual gas analyzer in the molecular-beam source region. The solid line is the (forward convolution) simulated TOF spectrum obtained using the center-of-mass frame translational energy distribution,  $P(E_T)$  of reaction (1), shown in Fig. 2. The good fit to both TOFs by the same  $P(E_T)$  indicates that Cl and NCO are “momentum-matched” and derive from the same dissociation process of  $\text{ClNCO}$ . It is noteworthy that the  $P(E_T)$  predicts the  $m/z = 42$  TOF of Fig. 1 well even at large values of the TOF where NCO is formed with the low  $E_T$  and hence high internal energy. This characteristic of the observations indicates that NCO does not dissociate before reaching the ionization region of the apparatus some  $100 \mu\text{s}$  after photolysis.

In carrying out the analysis of these experiments, we found that the use of literature thermochemistry for interpretation of  $P(E_T)$  of reaction (1) led to puzzling results. Specifically an apparent tendency to produce highly internally excited NCO with a concomitant lack of translational energy release and, more troubling, no evidence of NCO unimolecular decomposition when the molecule was apparently formed

above its spin-allowed dissociation limit. The dashed downward-pointing arrows in Fig. 2 show the apparent maximum,  $\epsilon_T^{\text{max}}$ , and minimum,  $\epsilon_T^{\text{min}}$ , translational energy release predicted from published thermochemistry. Observed reaction at a translational energy equal to  $\epsilon_T^{\text{max}}$  would correspond to formation of  $\text{Cl} + \text{NCO}$  with no internal energy in either product. Translational energy less than  $\epsilon_T^{\text{min}}$  would pro-

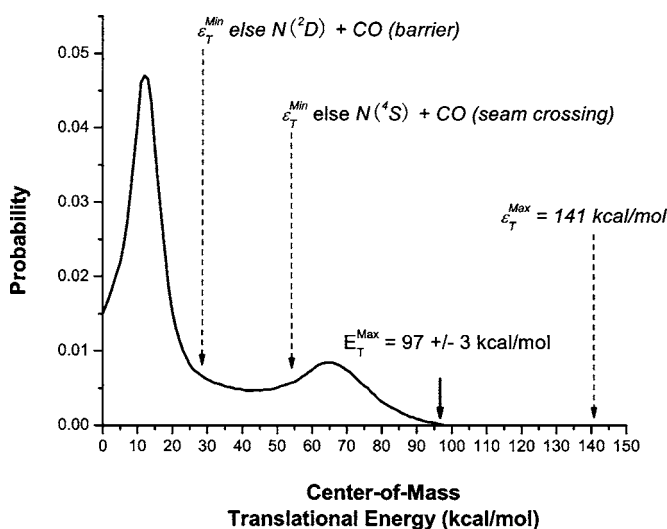


FIG. 2. Center-of-mass translational energy release distribution,  $P(E_T)$ , for the dominant photodissociation channel of chlorine-isocyanate,  $\text{ClNCO} \rightarrow \text{Cl} + \text{NCO}$ , at 193 nm. The observed maximum translational energy release,  $E_T^{\text{max}} = 97 \pm 3$  kcal/mol, yields an upper limit to the bond energy of  $D_0(\text{Cl}-\text{NCO}) = 51 \pm 3$  kcal/mol. From known heats of formation for Cl (Ref. 9) and NCO (Ref. 10)  $\Delta H_f(\text{ClNCO})$  is found to be  $8.5 \pm 3$  kcal/mol. These results are in good agreement with the ab-initio electronic structure calculations presented in Table I. The only previously available value,  $\Delta H_f(\text{ClNCO}) > 52.9$  kcal/mol (Ref. 8), implies a  $\epsilon_T^{\text{max}} > 141$  kcal/mol, and would mean that at translational energies below 27 kcal/mol, NCO is formed with sufficient internal energy for spin-allowed dissociation to  $\text{N}(^2\text{D}) + \text{CO}$  (Ref. 6). A doublet/quartet curve crossing has recently been identified (Ref. 7) that, again using the previous thermochemistry (Ref. 8), implies spin forbidden unimolecular dissociation of NCO at translational energies below 54 kcal/mol. No evidence of NCO dissociation is observed in this work.

TABLE I. Results of electronic structure theory. CCSD(T) calculations of Cl–NCO bond energies using different basis sets with increasing level of sophistication. Data are corrected for basis set superposition error (BSSE) and zero-point vibrational energy (ZPE). The complete basis set limit (CBS) is calculated after focal point analysis of the cc-*p*VxZ data (see text). All energies are in kcal/mol.

Basis set	$D_0(\text{Cl-NCO})^{\text{uncorr}}$	BSSE	ZPE	$D_0(\text{Cl-NCO})$
cc-pVTZ	52.64	-2.20	-1.83	48.61
aug-cc-pVTZ	54.26	-2.17	-1.82	50.27
cc-pVQZ	55.59	-0.89	-1.85	52.84
cc-pV5Z	57.11	-0.44	-1.85 <sup>a</sup>	54.82
CBS limit	58.16	0	-1.85 <sup>a</sup>	56.31

<sup>a</sup>The cc-pVQZ value is used.

duce NCO with enough internal energy to dissociate over the barrier to spin-allowed products,  $\text{N}(^2\text{D})+\text{CO}$ . The value of  $\epsilon_T^{\text{min}}$  which would access a theoretically predicted seam crossing to spin-forbidden dissociation is also shown.

In light of these puzzling implications, a review of the literature thermochemistry was undertaken. The presently recommended literature values of the relevant heats of formation are: for CINCO ( $\Delta H_f > 52.9$  kcal/mol),<sup>8</sup> for Cl ( $\Delta H_f = 28.992$  kcal/mol)<sup>9</sup> and for NCO ( $\Delta H_f = 30.5$  kcal/mol).<sup>10</sup> These values suggest a dissociation energy,  $D_0(\text{Cl-NCO})$  of less than 6 kcal/mol. Such a low bond energy is suspect on its face. Consider that  $\text{ClN}_3$  exhibits a dissociation energy of  $D_0(\text{Cl-N}_3) = 49$  kcal/mol<sup>1</sup> and that in a chemically similar pair,  $D_0(\text{H-NCO})$  is about 15% larger than  $D_0(\text{H-N}_3)$ . Thus one might reasonably postulate a value of  $D_0(\text{Cl-NCO})$  closer to 55 kcal/mol which is 12% larger than  $D_0(\text{Cl-N}_3)$ . It is also clear that any error in the thermochemistry must involve the CINCO heat of formation as the heats of formation of NCO and Cl appear secure, having been reproduced by multiple high-level experiments and confirmed by accurate electronic structure calculations.

In light of these internal inconsistencies, we are led to revise the literature value of  $\Delta H_f(\text{CINCO})$  by a simple analysis of the  $P(E_T)$  of Fig. 2. Here, we assume that the maximum observed release of translational energy,  $\epsilon_T^{\text{max}}$ , corresponds to formation of Cl and NCO with no internal energy. This assumption yields an upper bound to the value of  $D_0(\text{Cl-NCO}) = 51 \pm 3$  kcal/mol and  $\Delta H_f(\text{CINCO}) = 8 \pm 3$  kcal/mol.

The large disagreement with previous work, led us to seek confirmation by independent means. Thus, *ab initio* electronic structure theory was used to independently derive  $D_0(\text{Cl-NCO})$ . Table I shows the results of these calculations, carried out using conventional coupled cluster CCSD(T)<sup>11</sup> (coupled cluster singles and doubles with perturbative triples) treatment of electronic correlation and the (aug)-cc-*p*VxZ families of basis sets<sup>12</sup> with increasing levels of sophistication [ $x=3(\text{T})$ ,  $4(\text{Q})$ , and  $5$ ]. The geometries of CINCO and NCO were optimized at CCSD(T)/cc-*p*VTZ level of theory. Values at higher basis sets were obtained as a single-point calculation on the optimized cc-*p*VTZ geometry. The  $D_0(\text{Cl-NCO})$  energies were corrected for basis set superposition error (BSSE)<sup>13</sup> and zero-point vibrational energy (ZPE). As could be expected, BSSE decreases with increas-

ing basis set quality and becomes less than 0.8% for the highest quality basis sets used. All above calculations were performed using GAUSSIAN 03 program package.<sup>14</sup>

To evaluate the complete basis set limit (CBS) we performed focal point analysis<sup>15</sup> of the cc-*p*VxZ data. The Hartree-Fock energies were extrapolated using  $x=3, 4$ , and  $5$  and the exponential form of Feller *et al.*<sup>16</sup> The correlation energies were extrapolated using  $x=4$  and  $5$  and the integrated Schwartz expression.<sup>17</sup> The results are shown in the last row of Table I. As can be seen, the 1st principles electronic structure theory suggests a  $D_0(\text{Cl-NCO})$  value of 56.3 kcal/mol, in good agreement with the new experimental results of  $51 \pm 3$  kcal/mol.

The revised heat of formation and atomization energy allow comparison between six related molecules, revealing the magnitude of destabilization of azide with respect to the isoelectronic isocyanates, as shown in Fig. 3. At first we will examine hydrides in Figs. 3(a) and 3(b). The atomization energy of  $\text{HN}_3$  to the ground state atoms:  $\text{H}(^2\text{S})+3\text{N}(^4\text{S})$  is smaller by 109 kcal/mol than the atomization energy of  $\text{HNCO}$  to the ground state atoms:  $\text{H}(^2\text{S})+\text{N}(^4\text{S})+\text{C}(^3\text{P})+\text{O}(^3\text{P})$ . One might be tempted to consider this difference the fundamental azide versus isocyanate destabilization energy. However, since the CO bond energy (257 kcal/mol) is 31 kcal/mol larger than the  $\text{N}_2$  bond energy (226 kcal/mol), the difference in dissociation energy between  $\text{HN}_3 \rightarrow \text{HN} + \text{N}_2$  (50 kcal/mol) and that of  $\text{HNCO} \rightarrow \text{HN} + \text{CO}$  (128 kcal/mol) is a better measure of this so-called “azide destabilization.” An alternative analysis through  $\text{HNXY} \rightarrow \text{H} + \text{NXY} \rightarrow \text{H} + \text{N} + \text{XY}$  (where XY is  $\text{N}_2$  or CO) route shows that H–NNN bond is 22 kcal/mol weaker than the H–NCO bond, and the N–NN bond is 56 kcal/mol weaker than the N–CO bond. One clearly sees that the azide destabilization mainly originates from the weakness of the N–NN bond relative to the N–CO bond.

The situation is similar for the chloride,  $\text{ClN}_3$  versus CINCO, as shown in Figs. 3(c) and 3(d). The dissociation energy of  $\text{ClN}_3 \rightarrow \text{ClN} + \text{N}_2$  (7 kcal/mol) is 58 kcal/mol smaller than that of  $\text{CINCO} \rightarrow \text{ClN} + \text{CO}$  (65 kcal/mol). The weakness of the ClN–NN bond relative to the ClN–CO bond, “the azide destabilization,” is recognized here as well. An alternative analysis through  $\text{ClNXY} \rightarrow \text{Cl} + \text{NXY} \rightarrow \text{Cl} + \text{N} + \text{XY}$  (where XY is  $\text{N}_2$  or CO) route shows that Cl–NNN bond is only 2 kcal/mol weaker than the Cl–NCO bond and most of the azide destabilization is due to the fact that the N–NN bond is 56 kcal/mol weaker than the N–CO bond, as discussed above.

To understand the origin of the “azide destabilization,” the 78 kcal/mol difference in dissociation energy between  $\text{HN-N}_2$  (50 kcal/mol) and  $\text{HN-CO}$  (128 kcal/mol) and the 58 kcal/mol difference between  $\text{ClN-N}_2$  (7 kcal/mol) and  $\text{ClN-CO}$  (65 kcal/mol), we performed energy decomposition analysis<sup>18</sup> at the RHF/cc-*p*VTZ level using the GAMESS program package.<sup>19</sup> In this analysis the bonding stabilization energy (negative of the bond energy) is divided into three terms: electrostatic interaction, ES, exchange repulsion, EX, and orbital interaction, ORB. For detailed definition of these terms, the readers are referred to the original paper.<sup>18</sup> The electrostatic interaction, ES, represents the purely classical

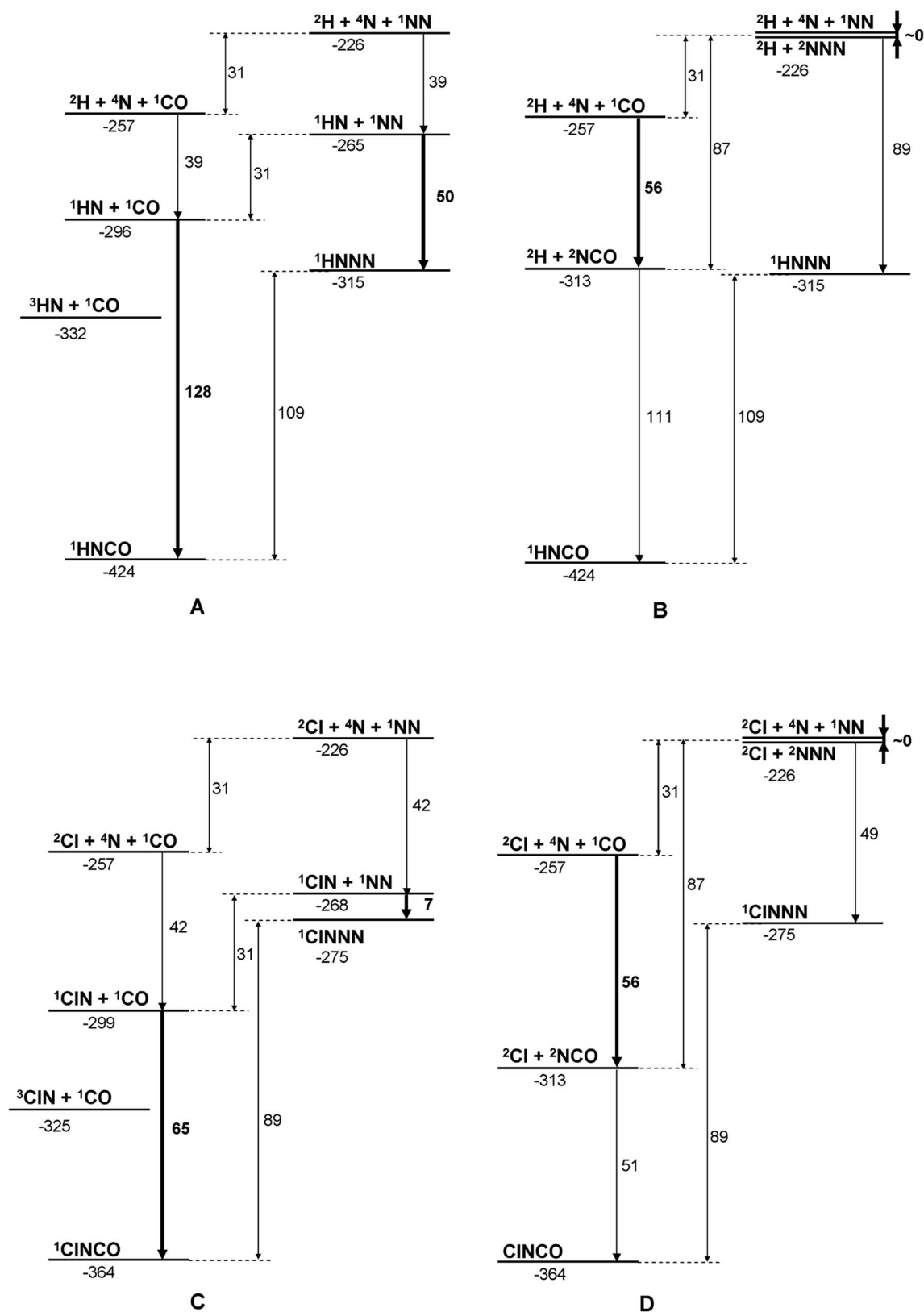


FIG. 3. Experimental energetics (in kcal/mol) of formation of HNX (XY=CO, N<sub>2</sub>) from a) HN and XY and b) H and NXY; and CIN (XY=CO, N<sub>2</sub>) from c) CIN and XY and d) Cl and NXY.

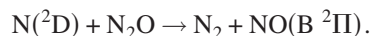
interaction between the charge distributions obtained from the wavefunctions of the individual fragments, HN and XY. The exchange repulsion, EX, is the repulsion energy originating from the requirement that the total wave function

made of the wave functions of individual fragments has to satisfy the Pauli principle. The orbital interaction, ORB, is everything else and due to the overall reorganization of orbitals including charge transfer and polarization.

The results of the energy decomposition analysis point out that the bonding between HN and CO at the HNCO equilibrium geometry has 261 kcal/mol larger exchange repulsion, 116 kcal/mol more attractive electrostatic interaction and 223 kcal/mol more attractive orbital terms than the bonding between HN and N<sub>2</sub> at the HN<sub>3</sub> equilibrium geometry. The larger values of all the attractive as well as repulsive components for HN–CO indicate that this interaction is “stronger” than the HN–NN interaction. This is reflected in the shorter N–CO distance in HNCO than the N–NN distance in HN<sub>3</sub>. One recognizes that  $\Delta\text{ORB}$  is more dominant than  $\Delta\text{ES}$  in HN–CO versus HN–NN difference. The  $\pi$  electrons in CO are polarized as  $^{+\delta}\text{C}-\text{O}^{-\delta}$  and create a situation where it is more favorable to make a dative bond by charge transfer from the filled sp lone pair orbital of HN(<sup>1</sup> $\Delta$ ) to the in-plane  $\pi$  orbital of CO in the bent H–N–CO configuration, while N<sub>2</sub> is homopolar and is less likely to form such a dative bond; this must be reflected in the more negative (attractive) ORB term for HN–CO compared to HN–NN, hence in a large negative  $\Delta\text{ORB}$ . With more attractive orbital interaction, the HN–CO distance will be smaller with a larger bond energy and all larger energy components than its HN–NN counterparts.

The analysis shows a similar picture for the 58 kcal/mol difference between CIN–N<sub>2</sub> (7 kcal/mol) and CIN–CO (65 kcal/mol). The bonding between CIN and CO at the CINCO equilibrium geometry has 131 kcal/mol larger exchange repulsion, 58 kcal/mol more attractive electrostatic interaction and 137 kcal/mol more attractive orbital terms than the bonding between CIN and N<sub>2</sub> at the CIN<sub>3</sub> equilibrium geometry. Again, the interaction is “stronger” in CIN–CO than in CIN–NN.

Finally, we comment on a possible problem with the previous derivation of  $\Delta H_f(\text{CINCO})$ . That work relied on an argument that 248-nm photolysis of CINCO produced large amounts of N(<sup>2</sup>D). The N(<sup>2</sup>D) was detected indirectly by observation of fluorescence emission resulting from the reactions:



By assuming that the N(<sup>2</sup>D) came from single-photon absorption of CINCO, a lower limit to  $\Delta H_f(\text{CINCO})$  could be extracted. Our results from the NSRRC show no evidence of one photon photochemistry leading to N(<sup>2</sup>D) even at the much higher available energy provided by a 193-nm photon. We presume that the previous work,<sup>8</sup> carried out at 50–100 mJ/cm<sup>2</sup> may have been influenced by multiphoton photochemistry.

Based on the thermochemistry derived in this work, we can assign the faster component of the  $P(E_T)$  in Fig. 2 to production of Cl+NCO(X). The assignment of the slower, high internal energy, component is still an unsolved problem. Several NCO electronic states, including cyclic-NCO, have energetics that can explain this peak. Therefore, the results of this work cannot definitely prove or disprove the possibility

of cyclic-NCO formation in CINCO photolysis at 193 nm. Further experimental and theoretical work will be needed to clarify this point.

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