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The Heats of Formation of *tert*-Butyl Isocyanide and Other Alkyl Isocyanides by Photoelectron Photoion Coincidence Spectroscopy

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Threshold photoelectron photoion coincidence (TPEPICO) spectroscopy has been used to investigate the dissociation energy of *tert*-butyl isocyanide (t-$C_4H_9NC^+$) ion. The 0 K dissociation limit of $CN^\bullet + C_4H_9^+$ (10.943 ± 0.010 eV) is determined from the breakdown diagram. The ionization energy of *tert*-butyl isocyanide is measured by threshold photoelectron spectra (TPES) and is 10.757 ± 0.005 eV. These values are used to obtain the 298 K heat of formation of *tert*-butyl isocyanide molecule (88.1 ± 3.7 kJ/mol). The 298 K heats of formation of CH_3CH_2NC and $(CH_3)_2CHNC$ are 144.8 ± 8 kJ/mol and 116.5 ± 8 kJ/mol, respectively, determined by a linear interpolation between the heats of formation of CH_3NC and t-C_4H_9NC. These results are in excellent agreement with density functional and ab initio theoretical values obtained from isomerization energies between the alkyl cyanides and the isocyanide heats of formation. Aside from CH_3NC, these are the first experimental heats of formation for the alkyl isocyanide molecules.

1. Introduction

It is remarkable that thermochemical compilations[1−9] list accurate values (±2 kJ/mol) for numerous alkylcyanides (RCN) but list only one member of the less stable isomeric alkyl isocyanides, which is CH_3NC. The reduced stability of the isocyanides is reflected in the formal charges on the carbon and nitrogen atoms. Whereas the formal charges in the RCN compounds are all zero, they are +1 and −1 for N and C in the isocyanides, respectively.

Although their heats of formation are not established, the alkyl isocyanides are an important class of compounds that are used as ligands in organometallic complexes[10,11] because of their sigma electron donation to the metal center and their ability to participate in π back-bonding. In addition, the isomerization between a variety of RCN ↔ RNC has been the subject of numerous experimental studies because of the simplicity of the reaction coordinate, which involves a simple rotation of the CN group.[12−16]

The mass spectrometry of the alkyl cyanides and isocyanides was studied several years ago by Heerma and de Ridder,[17] who noted that the mass spectra of the two isomeric species are quite different. In general, the RCN^+ ions dissociate via complex paths that yield products associated with rearrangement reactions, whereas the RNC^+ ions dissociate at low energies primarily via $H\bullet$ and $CN\bullet$ loss steps. That is, the higher energy isocyanides do not rearrange to the lower energy cyanides prior to dissociation.

In this study, we report on the threshold photoelectron photoion coincidence (TPEPICO) spectra of *tert*-butyl isocyanide. Previous mass spectral studies of this compound have shown that the lowest energy dissociation channel for this ion generates the *tert*-butyl ion and the $CN\bullet$ radical. If the two products have well-known heats of formation, an accurate measurement of the dissociation energy should permit us to determine the heat of formation of the starting molecule.

An approximate ionization energy (IE) of *tert*-butyl isocyanide by electron impact mass spectrometry was reported as 10.5 eV.[17] More recently, Wang et al.[15] found the ionization energy of *tert*-butyl isocyanide to be 10.82 eV by the much more reliable method of photoelectron spectroscopy. The only measurement of the dissociation onset to $C_4H_9^+ + CN\bullet$ was performed by Heerma and de Ridder,[17] who reported a value of 12.15 eV on the basis of variable energy electron impact ionization. No other products were reported. However, it is well known that the dissociation onsets measured by nonmonoenergetic electron impact ionization are very unreliable. Much more accurate dissociation onsets can be obtained by using threshold photoelectron photoion coincidence (TPEPICO) spectroscopy, one of the most precise methods to measure such thermochemical information.

In this project, we investigate the IE of *tert*-butyl isocyanide and 0 K dissociation limit (E_0) to $C_4H_9^+ + CN\bullet$ using TPEPICO. Recent experimental advances that suppress the contribution of "hot electrons" permit determining these onsets to a precision of better than 5 meV (0.5 kJ/mol).[18,19] These values are compared with ab initio and density functional theoretical calculations. Because the heats of formation of the $C_4H_9^+$ ion and the $CN\bullet$ radical are reasonably well known, we can relate the dissociation onset through the usual thermochemical cycle to obtain the heat of formation of *tert*-butyl isocyanide molecule.

2. Experimental and Theoretical Methods

A. Experimental Approach. The TPEPICO apparatus has been described in detail elsewhere.[19,20] Briefly, room-temperature sample vapor is introduced into the experimental chamber through a small stainless steel capillary pointing into the ionization region and then ionized with vacuum ultraviolet (VUV) light from a hydrogen discharge lamp dispersed by a 1-m-long normal incidence monochromator. The VUV wavelengths are calibrated by using the Lyman-α emission at 1215.688 Å, which is the most intense line in this spectrum. The ions and electrons are extracted in opposite directions with

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TABLE 1: Vibrational Frequencies Calculated at B3LYP/6-311++G(d,p) Level

reactant ion	vibrational frequencies
C_4H_9NC	174, 174, 214, 273, 273, 353, 353, 395, 514, 514, 699, 867, 928, 928, 972, 1057, 1057, 1237, 1248, 1248, 1402, 1402, 1433, 1474, 1488, 1488, 1501, 1501, 1519, 2203, 3036, 3036, 3043, 3107, 3107, 3111, 3115, 3116, 3116
$C_4H_9NC^{+}$ [a]	162, 162, 202, 267, 267, 315, 315, 362, 426, 426, **484**, 757, 913, 913, 963, 963, 985, 1147, 1215, 1215, 1382, 1382, 1423, 1431, 1468, 1468, 1475, 1475, 1513, 2300, 3028, 3028, 3042, 3101, 3101, 3111,3130, 3135, 3135
$C_4H_9^{+}$	53, 90, 193, 409, 410, 451, 750, 775, 829, 976, 994, 1002, 1110, 1292, 1301, 1337, 1347, 1358, 1409, 1423, 1437, 1496, 1500, 1505, 2942, 2949, 2973, 3040, 3060, 3062, 3151, 3152, 3159

[a] Vibrational frequencies of first local minimum. The reaction coordinate is shown with bold.

TABLE 2: 0 K Dissociation Limit (E_0), Bond Dissociation Energies, and Ionization Energies for *tert*-Butyl Isocyanide Ion

	E_0 (eV)	0 K BDE (eV)	IE (eV)
TPEPICO	10.943 ± 0.010	0.186 eV	10.757 ± 0.005
EI[a]	12.15	1.65	10.50
B3LYP/6-311++G(d,p)	10.76	0.01	10.75
CCSD(T)/ 6-311++G(2df,p)	11.04	0.37	10.68
G2	11.21	0.34	10.88

[a] Measured by Heerma and de Ridder.[17]

an electric field of 20 V/cm. The electrons are velocity focused[21] and collected by either a Burle Channeltron (located on the axis) or Burle multichannel plate (ring around the axis). Threshold electrons and energetic electrons with zero energy along the extraction axis (the hot electrons) are collected by the Channeltron, whereas energetic electrons with a few millielectronvolts perpendicular to the extraction axis are collected by the multichannel plate detector. By subtracting the coincidence spectrum obtained with the MCP from the TPEPICO spectrum, we obtain a hot electron free TPEPICO spectrum. The ions are accelerated to 100 eV in the first 5-cm-long accelerated region and travel 40 cm in the first drift region. Ions are then reflected by a reflectron and travel through another 35-cm-long second drift region before being collected at a multichannel plate ion detector. The electron and ion signals are used as start and stop pulses for measuring the ion time-of-flight (TOF). Typical electron and ion count rates are 50 electrons and 300 ions per second so that a complete TPEPICO TOF spectrum could be collected in 2−12 h. The TOF distributions obtained at each photon energy are used to obtain the fractional abundance of the precursor and the product ion (breakdown diagram). *tert*-Butyl isocyanide was acquired from Aldrich Chemical Co. and used without further purification. No impurities were detected in our TPEPICO mass spectra.

B. Theoretical Approach. The geometry and electronic energy of all molecules studied were calculated with several theoretical approaches including G2 methods,[22] density functional theory (DFT) with the Becke 3 parameter fit using the Lee, Yang, and Parr (B3LYP) functional[23,24] with a 6-311++G(d,p) basis set. This was followed by a single-point calculation using coupled-cluster methods[25] with singles, doubles, and perturbative triples excitation[26] (CCSD(T)) with 6-311++G(2df,p). The vibrational frequencies of *tert*-butyl isocyanide required for the analysis of the breakdown curve, as well as *tert*-butyl isocyanide cation, and *t*-$C_4H_9^{+}$ cation were calculated at the B3LYP/ 6-311++G(d,p) level and are listed in Table 1 without scaling. The potential energy surface along the $(CH_3)_3$-C−NC bond was scanned at the B3LYP/6-311++G(d,p) level with single-point CCSD(T)/6-311++G(2df,p) calculations performed at the extrema. The zero-point energy corrections are taken into account at the B3LYP/6-311++G(d,p) level. All calculations used the Gaussian03 ab initio package.[27]

TABLE 3: Thermochemical Results (kJ/mol) of Alkyl Isonitriles from This Study

species	$\Delta_f H°_{298K}$	B3LYP/ 6-311++G(d,p)	CCSD(T)[a]	G2
CH_3NC	173.2 ± 0.4[b]	174.6	175.5 175.1[c]	172.9
CH_3CH_2NC	144.8 ± 8.0	143.2	143.9	141.7
$(CH_3)_2CHNC$	116.5 ± 8.0	107.8	108.4	106.2
$(CH_3)_3CNC$	88.1 ± 3.7	77.2	77.4	94.6
$(CH_3)_3CNC^{+}$	1126.0 ± 3.7	1114.4	1107.8	1129.8

[a] 6-311++G(2df,p) basis set results. [b] Adjusted value of Baghal-Vayjooee.[41] [c] aug-cc-pVQZ basis set result.

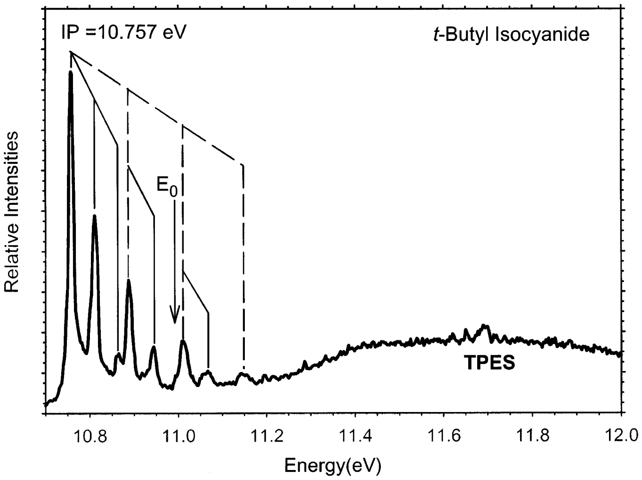

Figure 1. The threshold photoelectron spectrum of *tert*-butyl isocyanide between 10.7 and 12 eV. Two series of vibrational peaks (440 ± 50 cm^{-1} and 1050 ± 50 cm^{-1}) are excited in the ionization process and are indicated by the solid and dashed lines.

3. Results

The threshold photoelectron spectrum (TPES) of *tert*-butyl isocyanide is shown in Figure 1. The IE obtained from the peak is 10.757 ± 0.005 eV, which is considerably higher than 10.50 eV reported by Heerma and de Ridder[17] but is 60 meV lower than the photoelectron spectroscopy value of 10.82 eV reported by Wang et al.[15] The discrepancy between the TPES and PES values is somewhat surprising as the dominant peak is the 0−0 transition. The strong 0−0 transition implies that there is little change in the bond energies upon ionization. The broad peak starting at 11.2 eV and peaking at 11.6 eV is the second electronic state, which was also observed in the photoelectron spectrum by Wang et al.[15] It is interesting that the B3LYP/6-311++G(d,p) calculation predicts that there are two minima on the C_4H_9−NC^{+} surface, one in which the R−NC^{+} bond distance of 1.544 Å is similar to that in the neutral (1.446 Å), and the other isomer (lower by 0.24 eV at B3LYP/6-311++G(d,p) and higher by 0.02 eV at CCSD(T)/6-311++G(2df,p)) in which the R−NC^{+} bond has been stretched to 3.165 Å.

The Franck−Condon factors clearly favor the production of the conformer with the 1.544 Å C−N bond. On the basis of the strong 0−0 transition and the sharp structure that extends to 11 eV in the TPES of Figure 1, it is evident that this molecule is ionized to the first isomer and that there is little communication (slow intermolecular vibrational relaxation (IVR)) between these two states. The B3LYP/6-311++G(d,p) calculations also show that nearly all the positive charge is localized on the NC group in the first isomer (0.30, 0.53, and 0.17 Mulliken charges for C, N, *t*-C_4H_9, respectively), a consequence of the electron removal from the lone pair on the NC group. Eventually, the charge has to move from the NC group with its IE of 13.598 eV,[28] to the *tert*-butyl group with its much lower ionization energy of 6.70 ± 0.03 eV.[29] This is confirmed by the B3LYP/6-311++G(d,p) calculated charge distribution of the second isomer in which the charge is entirely localized on the *t*-$C_4H_9^+$ fragment (0.17, −0.13, and 0.96 Mulliken charges for C, N, *t*-C_4H_9, respectively). That is, a charge transfer takes place between the first and second geometry, which is also a step required for dissociation. The barrier for the charge transfer is calculated to be only 0.06 and 0.13 eV at the B3LYP/6-311++G(d,p) and CCSD(T)/6-311++G(2df,p) level of theory, respectively. This is rather surprising in view of the sharp structure that extends to over 0.3 eV. Our experimental IE of 10.757 ± 0.005 eV is in good agreement with our calculated theoretical values of 10.75, 10.88, and 10.68 eV at B3LYP/6-311++G(d,p), G2, and CCSD(T) levels of theory, respectively.

The TPES in Figure 1 shows that two vibrations are excited upon ionization, which are 440 ± 50 cm^{-1} and 1050 ± 50 cm^{-1}. Because only frequencies that change upon ionization are expected to be excited, we can attempt to identify these vibrations by looking for changes in the calculated frequencies for the neutral and ionic *tert*-butyl isocyanide. The vibrational frequencies for the neutral and ionic *tert*-butyl-isocyanide as well as the *tert*-butyl ion product, calculated with B3LYP/6-311++G(d,p) theory, are shown in Table 1. The comparison of the neutral and ionic frequencies shows that major changes occur for several vibrational frequencies, such as 514 → 426, 699 → 484, as well as 1057 → 963 and 1237 → 1147 cm^{-1}. These are quite close to the observed vibrational excitations in the TPES of Figure 1 of 440 ± 50 cm^{-1} and 1050 ± 50 cm^{-1}. Because we have difficulty in distinguishing differences of 50 cm^{-1}, we cannot assign the 440 cm^{-1} progression in Figure 1 to one or the other, and indeed it could be due to both of these vibrations.

The DFT calculations of the vibrational modes show that two of the frequencies (484 and 1147 cm^{-1}) involve the C−NC stretch along with complicated motions of the methyl groups, which cause the *tert*-butyl group to become planar. In particular, the 484 cm^{-1} mode looks like the reaction coordinate for dissociation. If this mode is really the reaction coordinate, how is it possible for the structure to be so well defined even above the ion's dissociation energy, shown as an arrow in Figure 1? One explanation is that the reaction coordinate (484 cm^{-1} mode) is excited to only the $v = 2$ level, which is below the dissociation limit. If the higher frequency mode is not strongly coupled to dissociation, the TPES peak could be sharp even above the dissociation limit. Another explanation invokes the participation of two electronic states. If the electron is originally removed from the lone pair on the NC group, a charge exchange is required for dissociation, which transfers the charge to the *tert*-butyl group. If this curve-crossing step is sufficiently slow, the TPES structure could be sharp even above the dissociation limit.

The breakdown curve of *tert*-butyl isocyanide is shown in Figure 2. The *tert*-butyl isocyanide ion dissociates to $C_4H_9^+$ + CN• at an energy just above the ionization energy. The fractional abundance of the *tert*-butyl isocyanide parent ion drops to zero at 10.95 eV and is replaced by the $C_4H_9^+$ product ion. The solid lines are the calculated breakdown diagram in which the neutral *tert*-butyl isocyanide internal energy distribution, P(E), is taken into account. All ions that have an energy in excess of the dissociation limit are assumed to dissociate immediately. A rapid reaction at threshold is confirmed by our TOF distributions that exhibit only symmetric *tert*-butyl TOF peaks. Because the ion internal energy is a sum of the photon energy plus the neutral internal energy, the daughter and parent ion curves ($B_d(h\nu)$ and $B_p(h\nu)$, respectively) are given by eqs 1 and 2:

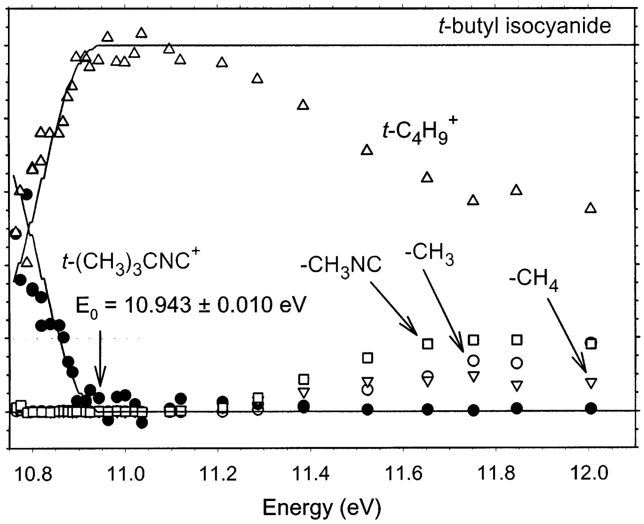

Figure 2. Breakdown curve of *tert*-butyl isocyanide is shown as a function of photon energy. Closed and open symbols are the experimental fractional abundance of parent and daughter ions, respectively. Lines are the best fit to the experimental data using eqs 1 and 2.

$$B_d(h\nu) = \int_{E_0-h\nu}^{\infty} \mathrm{P(E)}dE \; for\; h\nu < E_0 \; (B_d(h\nu) = 1 \; for\; h\nu > E_0) \quad (1)$$

$$B_p(h\nu) = \int_{0}^{E_0-h\nu} \mathrm{P(E)}dE \; for\; h\nu < E_0 \; (B_p(h\nu) = 0 \; for\; h\nu > E_0) \quad (2)$$

The best fit of the experimental breakdown curve, shown in Figure 2, is obtained when the E_0 is set at 10.943 ± 0.010 eV. This is more than 1 eV lower than the 12.15 eV reported in electron impact study by Heerma and de Ridder.[17] The other products observed in this study are CH_4, CH_3, and CH_3NC loss from the *t*-$C_4H_9NC^+$ ion. Although it is possible to obtain thermodynamic information from fitting higher energy products, we choose not to do so because our primary focus is to obtain the heat of formation of *tert*-butyl isocyanide. These ions appear well above the E_0 of $C_4H_9^+$ ion and thus do not interfere with the production of $C_4H_9^+$ ion at low energies. The calculated E_0 values for CN• loss are 10.76, 11.21, and 11.04 eV using B3LYP/6-311++G(d,p), G2, and CCSD(T)/6-311++G(2df,p) levels of theory.

The 0 K bond dissociation energy (BDE) of ionized *tert*-butyl isocyanide of 0.186 eV is obtained by subtracting the IE from E_0. The low bond energy is a direct consequence of the stable *t*-$C_4H_9^+$ ion. Although the agreement with our experiment is not perfect, theory supports the weak bond energies (0.01, 0.37, and 0.34 eV at B3LYP/6-311++G(d,p), CCSD(T)/6-311++G(2df,p), and G2 theory levels, respectively). An important point is that the calculated bond dissociation energies at the highest levels of theory are more than 0.23 eV higher than the previously mentioned isomerization barriers (0.06 and 0.13 eV). In addition, the experimental bond energy of 0.186 eV is also higher than the calculated isomerization barriers. This leads us to conclude that the measured dissociation limit corresponds to the dissociation asymptote and not to a barrier along the dissociation path.

4. t-C_4H_9NC and t-$C_4H_9NC^+$ Heats of Formation

The experimentally determined E_0 can now be used to determine the 0 and 298 K heats of formation of *tert*-butyl isocyanide molecule. To do so, it is necessary to know the ancillary heats of formation of the t-$C_4H_9^+$ ion and CN• radical. The most accurate 298 K heat of formation of $C_4H_9^+$ can be obtained from the proton affinity of isobutene, which is defined by the following reaction.

$$(CH_3)_2CCH_2 + H^+ \rightarrow (CH_3)_3C^+ \tag{3}$$

The proton affinity of isobutene has been carefully studied by temperature-dependent equilibrium studies in a high-pressure mass spectrometer by Szulejko and McMahon[30,31] and is 802.1 ± 2.1 kJ/mol, which is in excellent agreement with ab initio result of Smith and Radom.[32] By using the heat of formation of *iso*-butane, −16.9 ± 0.9 kJ/mol,[3] and H^+, 1530 kJ/mol,[28] the heat of formation of the t-$C_4H_9^+$ ion is 711.0 ± 2.3 kJ/mol. This value is in excellent agreement with the dissociative ionization of supersonically cooled beam of *tert*-butyl iodide of 711 ± 3.6 kJ/mol reported by Keister et al.,[33] as well as the 711.4 ± 1.1 kJ/mol reported by Traeger,[34] on the basis of a photoionization study of isobutane. Because three independent measurements agree to within 1 kJ/mol of each other, the heat of formation of the t-$C_4H_9^+$ is well established.

The heat of formation of the CN• radical is listed in the NIST Webbook as 435.14 kJ/mol.[28] However, this number is not without its controversy. The two methods used to obtain the CN• heat of formation have been through the bond energies of HCN and NCCN. The best value for HCN has been obtained by Cook et al.[35] who reported a bond energy of 43 710 ± 70 cm^{-1} (522.9 ± 0.8 kJ/mol). Unfortunately, the heat of formation of the HCN molecule listed in several compilations is controversial. Chase,[36] Wagman et al.,[37] and the NIST Webbook[28] all list the HCN heat of formation as 135.4 kJ/mol, but only Chase includes an error limit, which is ±8 kJ/mol. Two independent studies have suggested a revision of this energy. On the basis of electron affinity and gas-phase acidity measurements of several H_xCN_y species, Clifford et al.[38] concluded that the 0 K heat of formation of HCN should be revised downward to 129.3 ± 3 kJ/mol so that the photodissociation results of NCCN[39] would be consistent with the electron affinity measurements. The cyanogens (NCCN) heat of formation seems to be much better established than the HCN heat of formation. Pedley lists a $\Delta_f H°_{298K}$ (NCCN) of 306.7 ± 0.8 kJ/mol,[3] while Chase lists it at 309.0 ± 1.8 kJ/mol,[36] which yields an average value of 307.8 ± 2.0 kJ/mol. In support of a lower HCN heat of formation, a high-level theoretical study by Martin[40] also suggested an HCN heat of formation of 129.9 ± 1 kJ/mol. With this lower HCN heat of formation, we can obtain the CN• radical heat of formation from the following two cycles:

$$HCN \rightarrow H + CN\bullet \quad D_o = 522.9 \pm .8\ \text{kJ/mol}^{35}$$
$$\Delta_f H°_{0K}(CN\bullet) = 436.2 \pm 3\ \text{kJ/mol}$$

$$NCCN \rightarrow 2CN\bullet \quad D_o = 563.5 \pm 2\ \text{kJ/mol}^{39}$$
$$\Delta_f H°_{0K}(CN\bullet) = 434.8 \pm 3\ \text{kJ/mol}$$

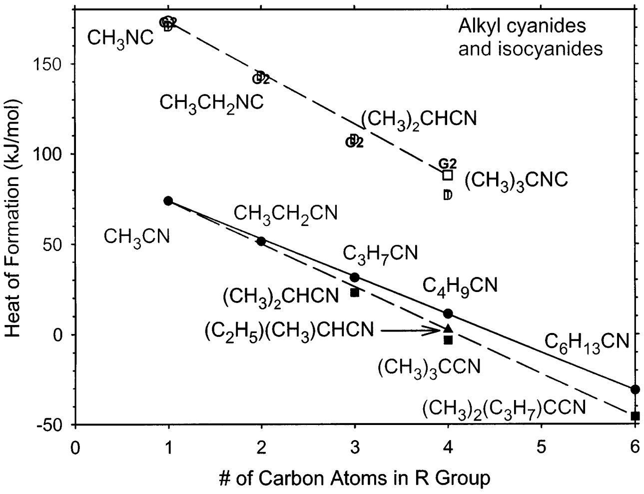

Figure 3. Heats of formation of nitriles (RCN) and isonitriles (RNC) plotted against the number of carbon atoms in the R group. Dashed lines are drawn through the branched R groups, whereas the solid line is through the straight-change R group nitriles. The symbols T, D, and G2 are the theoretical heats of formation calculated with the CCSD(T), B3LYP, and G2 theories.

For the cyanogen cycle, we assume an NCCN 0 K heat of formation of 306.0 ± 2 kJ/mol.

Because our experiment yields a 0 K E_0, the t-$C_4H_9^+$ ion heat of formation needs to be converted to 0 K, which is accomplished by eq 4:

$$\Delta_f H°_{0K}\,(A) = \Delta_f H°_{298K}\,(A) - [H°_{298K} - H°_{0K}](A) + [H°_{298K} - H°_{0K}](\text{elements}) \tag{4}$$

where the $[H°_{298K} - H°_{0K}]$ function is determined by using the frequencies provided at B3LYP/6-311++G(d,p) level, and "elements" refers to the sum of the elements in their standard states. The latter values are 8.468, 1.050, and 8.669 kJ/mol for H_2, C, and N_2, respectively.[37] This yields a 0 K heat of formation of t-$C_4H_9^+$ ion of 734.2 ± 2.3 kJ/mol.

The 0 K heat of formation of *tert*-butyl isocyanide is given by eq 5:

$$\Delta_f H°_{0K}\,(C_4H_9NC) = \Delta_f H°_{0K}\,(C_4H_9{}^+) + \Delta_f H°_{0K}\,(CN\bullet) - AE_{0K} \tag{5}$$

which yields a $\Delta_f H°_{0K}$(*tert*-butyl isocyanide) of 113.9 ± 3.7 kJ/mol using the average $\Delta_f H°_{0K}$(CN•). From eq 4, the 298 K heat of formation of *tert*-butyl isocyanide is then 88.1 ± 3.7 kJ/mol. By simply adding the ionization energy to the neutral heats of formation, we obtain the 0 K and 298 K t-$C_4H_9NC^+$ heats of formation of 1151.8 ± 3.7 kJ/mol and 1126.0 ± 3.7 kJ/mol, respectively.

5. Comparison to Other Cyano Compounds

The 298 K heats of formation in kJ/mol of CH_3CN (74.0),[4] C_2H_5CN (51.46),[5] n-C_3H_7CN (31.2),[8] n-C_4H_9CN (11.1),[6] $(CH_3)_2$-$CHCN$ (22.8),[5] $(C_2H_5)(CH_3)HCN$ (2.4),[7] $(CH_3)_3CN$ (−3.3),[5] n-$C_6H_{13}CN$ (−31),[9] and $(CH_3)_2(C_3H_7)CCN$ (−45.8)[7] are plotted in Figure 3 as a function of the number of carbon atoms in the R group. These heats of formation exhibit a remarkable linearity with increasing numbers of carbon atoms in the R group. The heats of formation are slightly dependent on the number of R groups attached on the α-carbon atom that binds to CN (i.e., $(CH_3)_3CN$ < $(C_2H_5)(CH_3)HCN$ < C_5H_9CN). Two linear interpolations are thus made between CH_3CN and $(CH_3)_2(C_3H_7)CCN$ and between CH_3CN and n-$C_6H_{13}CN$. The first line fits the heats of formation of all straight-chain nitriles whereas the second line fits the heats of formations of all nitriles with the maximum number of R-groups on the α-carbon atom.

Unlike the alkyl nitriles, the heats of formation of isonitrile molecules are largely unknown. The only isocyanide heat of formation available in the literature is that of CH_3NC. In addition, we now have a value for the $\Delta_f H°[(CH_3)_3CNC]$ measured in this work. The heat of formation for CH_3NC was experimentally measured from the isomerization reaction of CH_3CN and CH_3NC using calorimetry.[41] When this enthalpy of isomerization of 99.2 ± 0.6 kJ/mol is added to the heat of formation of CH_3CN, we obtain a CH_3NC heat of formation of 173.2 ± 0.7 kJ/mol. This value differs from the original value of 172.9 ± 1.0 kJ/mol listed by Baghal-Vayjooee et al.[41] because these authors used an old and inaccurate value 73.7 kJ/mol for the CH_3CN heat of formation. The 1986 Pedley compilation[2] lists the CH_3CN heat of formation as 64.3 ± 7.2 kJ/mol; however, the 1994 edition[3] lists it as 74.0 ± 0.3 kJ/mol. The higher experimental value of 74.0 kJ/mol is also supported by recent calculations of Mayer et al.[42] The difference in the heats of formation for CH_3NC and *t*-$(CH_3)_3CNC$ of 85.1 kJ/mol is slightly larger than the corresponding value for the nitrile compounds, 77.3 kJ/mol. But, by assuming the heats of formation of isonitrile molecules also decrease linearly as the number of carbon atoms increase, the suggested 298 K heats of formation for CH_3CH_2NC and $(CH_3)_2CHNC$ are 144.8 and 116.5 ± 8 kJ/mol by linear interpolation. $(CH_3)_2CHNC$ is chosen over C_3H_7NC because the line is connected to the heats of formation of $(CH_3)_3CNC$, which has three R-groups on the α-carbon atom.

To test these heats of formation, we performed theoretical calculations for the isomerization reaction between nitrile and isonitrile neutrals at 298 K.

$$\mathrm{RCN} \rightarrow \mathrm{RNC} \text{ where } \mathrm{R} = \mathrm{CH_3, CH_3CH_2, (CH_3)_2CH, (CH_3)_3C} \quad (6)$$

For CH_3CN and CH_3NC neutrals, single-point CCSD(T) calculations were performed using 6-311++G(2df,p) and the diffuse function augmented correlation consistent basis set[43] (aug-cc-pVTZ and aug-cc-pVQZ) with a geometry optimized at B3LYP/6-311++G(d,p) level. The thermal energy corrections are also taken into account at the B3LYP/6-311++G(d,p) level. The heats of isomerization are 113.4, 113.0, 112.2, 112.4, 99.8, 101.5, 100.9, 101.1, 98.9, and 100.6 kJ/mol for MP2/ 6-311++G(d,p), MP2/6-311++G(2df,p), MP2/aug-cc-pVTZ, MP2/aug-cc-pVQZ, CCSD(T)/6-311++G(d,p), CCSD(T)/6-311++G(2df,p), CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ, G2, and B3LYP/6-311++G(d,p) levels, respectively. By adding the heat of reaction to the known 298 K heats of formation of CH_3CN, the heats of formation of CH_3NC are 187.4, 187.0, 186.2, 186.4, 173.8, 175.5, 174.9, 175.1, 172.9, and 174.6 kJ/mol calculated at the various levels, respectively. The use of larger polarization or correlation consistent basis sets does not affect the heat of formation. It is evident that the MP2 calculations are more than 10 kJ/mol higher than CCSD(T) results even with aug-cc-pVQZ basis set. Therefore, higher order correlation terms must be included for calculation of accurate heats of isomerization. Surprisingly, the relatively inexpensive B3LYP/6-311++G(d,p) results differ by only 0.5 kJ/mol from the CCSD(T)/aug-cc-pVQZ values. Aside from the MP2 values, the theoretical results are within 2 kJ/mol of the known heat of formation of CH_3NC, 173.2 ± 0.7 kJ/mol, and are in good agreement with theoretical heat of formations, 178.6 kJ/mol, derived from atomization scheme using CBS−RAD level of theory.[42]

The calculated 298 K heats of formation for CH_3CH_2NC and $(CH_3)_2CHNC$ are 141.7 and 106.2 kJ/mol for G2 theory, 143.9 and 108.4 kJ/mol at CCSD(T)/6-311++G(2df,p) level of theory, and 143.2 and 107.8 kJ/mol at B3LYP/6-311++G(d,p) level of theory. These values are in excellent agreement with our suggested 298 K heat of formations of 144.8 ± 8 and 116.5 ± 8 kJ/mol for CH_3CH_2NC and $(CH_3)_2CHNC$, respectively. In addition to the CH_3CN/CH_3NC study, Baghal-Vayjooee et al.[41] also measured the ethyl cyanide to isocyanide isomerization enthalpy. However, those results are not as reliable as CH_3CN/CH_3NC results because the conversion was not as complete as in the methyl case. They reported the isomerization enthalpy to be 90.0 ± 4.2 kJ/mol. By adding this value to the known heat of formation of CH_3CH_2CN, we obtain the heat of formations of CH_3CH_2NC, 141.4 ± 4.2 kJ/mol. This value is also in excellent agreement with our suggested heat of formation. Finally, the calculated heats of formation of $(CH_3)_3CNC$ are 94.6, 77.4, and 77.2 kJ/mol for G2, CCSD(T)/6-311++G(2df,p), and B3LYP/6-311++G(d,p) levels of theory, respectively, the average of which is close to our experimental value of 88.1 ± 3.7 kJ/mol.

The excellent agreement between the calculated and experimental values for the CH_3NC and *t*-C_4H_9NC heats of formation and the linear relationship between the heats of formation and the number of carbon atoms means that the isonitrile heats of formation are now known to within at least 8 kJ/mol.

6. Conclusion

Threshold photoelectron photoion coincidence (TPEPICO) spectroscopy is used to measure the 0 K dissociation onset for the CN• loss reaction from ionized *tert*-butyl isocyanide. This is the lowest energy dissociation reaction and is observed to dissociate rapidly so that the onset can be used to relate reactant and product heats of formation. At higher energies, several other products are observed. To obtain the E_0 of the primary $C_4H_9^+$ ion, the experimental breakdown curve is fitted by varying a single parameter, the 0 K dissociation energy E_0. The best fit was obtained with an E_0 of 10.943 ± 0.010 eV. The analysis includes the thermal energy distribution of the reactant *tert*-butyl isocyanide. The IE of *tert*-butyl isocyanide is determined by threshold photoelectron spectroscopy to be 10.757 ± 0.005 eV.

Combining our experimental results with known heats of formation of *t*-$C_4H_9^+$ and CN•, we obtain a 298 K heat of formation of *tert*-butyl cyanide neutral of 88.1 ± 3.7 kJ/mol, and ion of 1126.0 ± 3.7 kJ/mol, through the usual thermodynamic cycle. Because the heats of formation of nitriles and isonitriles show a linear dependence on the number of carbon atoms in the alkyl group, linear interpolation is used to obtain suggested 298 K heats of formation of 144.8 ± 8 and 116.5 ± 8 kJ/mol for CH_3CH_2NC and $(CH_3)_2CHNC$, respectively. The heats of formation of all isonitriles are in good agreement with our theoretical values.

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