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Thermochemical Studies of Benzoylnitrene Radical Anion: The N−H Bond Dissociation Energy in Benzamide in the Gas Phase

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The thermochemical properties of benzoylnitrene radical anion, $C_6H_5CON^-$, were determined by using a combination of energy-resolved collision-induced dissociation (CID) and proton affinity bracketing. Benzoylnitrene radical anion dissociates upon CID to give NCO^- and phenyl radical with a dissociation enthalpy of 0.85 ± 0.09 eV, which is used to derive an enthalpy of formation of 33 ± 9 kJ/mol for the nitrene radical anion. Bracketing studies with the anion indicate a proton affinity of 1453 ± 10 kJ/mol, indicating that the acidity of benzamidyl radical, C_6H_5CONH, is between those of benzamide and benzoic acid. Combining the measurements gives an enthalpy of formation for benzamidyl radical of 110 ± 14 kJ/mol and a homolytic N−H bond dissociation energy in benzamide of 429 ± 14 kJ/mol. Additional thermochemical properties obtained include the electron affinity of benzamidyl radical, the hydrogen atom affinity of benzoylnitrene radical anion, and the oxygen anion affinity of benzonitrile.

Introduction

The knowledge of the bond dissociation energy of a molecule plays a significant role in investigation of the structure, energetics, and reactivity of that particular molecule.[1,2] However, direct measurement of the energies required to break chemical bonds can be challenging, and indirect approaches are commonly utilized instead. Therefore, bond dissociation energies are often determined by using reactivity-based methods, such as from the kinetics of atom-transfer reactions[3] or ion-based thermochemical measurements.[4]

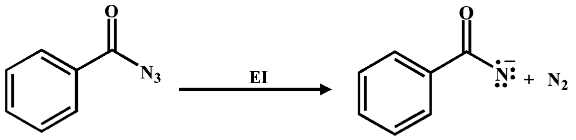
An advantage of ion-based methods is the flexibility they provide. For example, C−H bond dissociation enthalpies (BDEs) can be obtained by using either positive ion or negative ion approaches, with the familiar relationships shown in eqs 1a,b, where IE refers to the ionization energy, EA is the electron affinity, ΔH_{acid} is the gas-phase acidity, and $\mathrm{AE}(\mathrm{R}^+,\mathrm{H})$ is the appearance energy of R^+ upon activation of RH.[1,5]

$$\mathrm{BDE}(\mathrm{R{-}H}) = \mathrm{AE}(\mathrm{R}^+,\mathrm{H}) - \mathrm{IE}(\mathrm{R}) \tag{1a}$$

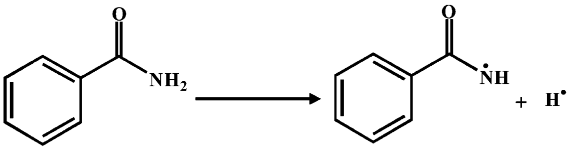
$$\mathrm{BDE}(\mathrm{R{-}H}) = \Delta H_{\mathrm{acid}}(\mathrm{RH}) + \mathrm{EA}(\mathrm{R}) - \mathrm{IE}(\mathrm{H}) \tag{1b}$$

However, there are many possible ionic approaches for determining BDEs besides those in eqs 1a,b.[6] For example, the BDE in a molecule RH can instead be derived from negative ion approaches involving the hydride affinity of R and electron affinity of RH, or the $\mathrm{R^-{-}H}$ BDE and the electron affinity of R, or using a positive ion approach involving the ionization energy of RH and the proton affinity of R. Similarly, the BDE could ultimately be calculated directly by measuring the enthalpies of formation of R and/or RH.

In this work, negative ion chemistry is used to determine the gas-phase N−H BDE in benzamide. Although amide N−H bonds are important in biological systems, studies of the strengths of the N−H bonds are limited. Bordwell and co-workers[7−9] have determined the N−H BDEs for amides in dimethyl sulfoxide (DMSO) solution, but gas-phase measurements are available for only the simplest amide molecules.[10] In this study, we report the generation of benzoylnitrene radical anion, $C_6H_5CON^-$ (**1**⁻), by electron ionization of benzoylazide (eq 2). The benzoylnitrene radical anion is expected to have an interesting electronic structure because it is essentially a benzoate ion in which one of the oxygen atoms has been replaced by a nitrogen atom. From thermochemical studies of ion **1**⁻, we obtain the enthalpy of formation of the benzamidyl radical, **2**, from which we calculate the N−H bond dissociation energy of the benzamide, **3** (eq 3). The thermochemical measurements moreover allow for the determination of other thermochemical properties for the sequential decomposition of benzamide.[2]



1⁻ (2)



3 **2** (3)

Experimental Section

All gas-phase experiments were carried out using a flowing afterglow−triple quadrupole mass spectrometer described previously.[11,12] The benzoylnitrene radical anion (**1**⁻) was generated in the ion source by 70 eV electron ionization of benzoylazide ($PhCON_3$). The ions were carried through the flow tube by helium buffer gas (P = 0.400 Torr; helium purity, 99.995%, with a flow rate of 190 cm^3(STP)/s). Ion/molecule reactions used to bracket the proton affinity of the ion were carried out by adding head vapors of neutral samples downstream in the flowing afterglow. Ions in the flow tube are extracted through a 1 mm nose cone orifice into a differentially pumped triple quadrupole mass analyzer.

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Collision-induced dissociation (CID) studies were carried out by selecting the ion with the desired mass-to-charge ratio in the first quadrupole. Subsequently the ions are injected into the second quadrupole (q2) where they undergo collisions in a collision cell containing argon. The collision energy was controlled by the q2 pole offset voltage, with the energy zero determined by retarding potential analysis. Reactant and fragment ions produced by CID were extracted into the third quadrupole and detected with a conversion dynode and an electron multiplier operated in pulse counting mode.

Dissociation Energy Measurements and Data Analysis. The absolute cross-sections for product ion formation during the CID were calculated using $\sigma_p = I_p/INl$, where I_p and I are the intensities of the product and the reactant, respectively, N is the number density of the target, and l is the effective length of the collision cell. The effective path length is calibrated to be 24 ± 4 cm on the basis of the reference reaction between Ar^+ and D_2.[13] The CID cross-sections were measured at different pressures and extrapolated to zero pressure before the analysis and correspond to single-collision values. The center-of-mass collision energies (E_{CM}) were calculated by using $E_{CM} = E_{lab}[m/(M + m)]$, where m and M are the masses of the target and ion, respectively, and E_{lab} is the collision energy in the laboratory frame.

The energy-resolved cross-sections are fit to the model shown in eq 4,[14−16] where E is the center-of-mass collision energy of the parent ion, g_i is the fraction of ions with the internal energy E_i, E_0 is the 0 K dissociation energy, n is an adjustable parameter that reflects the energy deposition in the collision,[17] and σ_0 is a scaling factor. The data were modeled to minimize the deviation between the model eq 4 and the steeply rising portion of the appearance curve just above the threshold. The parameter P_i in eq 4 is the probability that the ion with the given internal energy will dissociate on the instrumental time scale.[18] The dissociation rate is calculated using the RRKM approach. The transition-state properties were calculated assuming a product-like, orbiting (loose) transition state in the phase-space limit.[18] The vibrational frequencies and rotational constants required to estimate the internal energy of the ion and transition-state properties were calculated at the B3LYP/6-31+G* level of theory.[19] In the present system, changing the transition-state properties had no measurable effect on the optimized parameters, indicating that the reaction occurs rapidly on the instrumental time scale with little kinetic shift. Therefore, the choice of transition state does not affect the measured dissociation energy. The quantity E_0 was converted to the 298 K ΔH value by using the integrated heat capacities of reactants and products, estimated from calculated vibrational frequencies. All analysis was carried out using the CRUNCH program.[13−15,20,21]

$$\sigma(E) = \sigma_0 \sum_i P_i\, g_i(E + E_i - E_0)^n/E \tag{4}$$

Materials. Benzoylazide was synthesized by literature procedures.[22] All the other reagents were used as received, except helium, which was purified through a liquid nitrogen trap containing molecular sieves. Although the 1,2,3-triazole available from Aldrich is labeled as the 1H tautomer, microwave spectroscopy studies[23] have shown that the 2H to 1H tautomer ratio is 1000:1 at room temperature in the gas phase, and it is likely the 2H isomer that is the reactive species in our experiments. *CAUTION!: Acylazides are potentially explosive and should always be handled with proper precautions.* We have not encountered any problems with benzoylazide in this work, but it is still handled with protection.

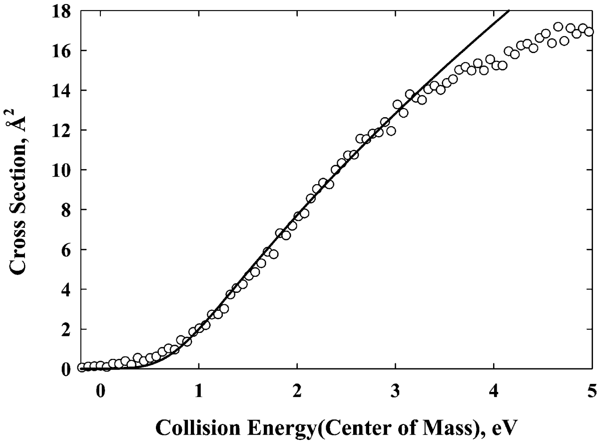
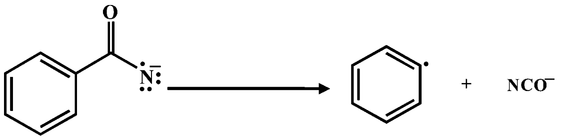


Figure 1. Cross-sections for formation of NCO^- upon collision-induced dissociation of benzoylnitrene radical anion, **1**$^-$, along with the analytical fit to the data, obtained using parameters described in the text.

Results

Ion Generation. Alkylazides have been utilized previously in gas-phase studies as precursors for methyl- and phenylnitrene radical anions.[24−27] Similarly, ionization of benzoylazide in the flowing afterglow gives m/z 119, benzoylnitrene radical anion, in abundant yield. Additional products include an ion with m/z 42, likely corresponding to isocyanate anion (NCO^-), with an intensity that is ~10% of that of m/z 119 ion and phenyl anion, m/z 77, with a relative intensity of ~5%. An additional product is also observed at m/z 151 and likely results from the addition reaction of ion **1**$^-$ with background O_2.

CID of Benzoylnitrene Radical Anion. Collision-induced dissociation of **1**$^-$ results in formation of isocyanate ion, m/z = 42, as the only ionic product (eq 5). Cross-sections for formation of m/z 42 as a function of center-of-mass collision energy are shown in Figure 1, along with the analytical fit to the data obtained by using the processes described in the experimental section. The optimal fitting parameters are $n = 1.5 \pm 0.1$ and $E_0 = 0.82 \pm 0.09$ eV, where the uncertainty includes the deviation of values obtained from replicate experimental trials and a 0.15 eV (laboratory frame-of-reference) uncertainty due to uncertainty in the absolute energy scale. The measured dissociation energy corresponds to a 298 K ΔH value of reaction 0.85 ± 0.09 eV (82 ± 9 kJ/mol). The ground state of **1**$^-$ is calculated to be $^2A'$, such that the dissociation is spin- and symmetry-allowed and the dissociation reaction should occur with little or no barrier in excess of the reaction exothermicity. Therefore, the measured dissociation can be equated with the bond dissociation energy.



(5)

Because the enthalpies of formation of the dissociation products are known, the bond dissociation enthalpy can be used to determine the enthalpy of formation of the benzoylnitrene radical anion. By using the measured value along with the enthalpies of formation listed in Table 1, the 298 K enthalpy of formation of **1**$^-$ is found to be 33 ± 9 kJ/mol.

Proton Affinity Studies of Benzoylnitrene Radical Anion. The proton affinity of **1**$^-$ was measured by using the bracketing approach. Although protonation can occur at either oxygen or

TABLE 1: Supplemental Thermochemical Data Used in This Work (298 K Values in kilojoules per mole)

compound	$\Delta H_{f,298}$	ΔH_{acid}	ref
phenyl radical, C_6H_5	337 ± 2		5, 20
phenyl anion, $C_6H_5^-$	231 ± 2		20
hydrogen isocyanate, HNCO	−119 ± 5 [a]	1428 ± 6 [b]	42, 43
isocyanate ion, NCO^-	−221 ± 4 [c]		derived
benzamide, C_7H_7NO	−101 ± 1	1481 ± 9	36, 42
benzoic acid, $C_7H_6O_2$	−295 ± 2	1423 ± 9	36, 42
hydrogen atom, H	218.0		6
proton, H^+	1530.1		6
benzonitrile, C_7H_5N	219 ± 8		42
atomic oxygen anion, O^-	108		36

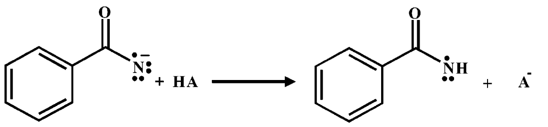
[a] Calculated by correcting the 0 K value reported in ref 43 to 298 K using the correction factor described in ref 44. [b] Obtained by using the 0 K value obtained using refs 43 and 45 and the temperature correction calculated at the CCSD(T)/aug-cc-pVTZ level of theory.[46] [c] Calculated by using the enthalpy of formation and gas-phase acidity of HNCO. The 298 K value is the same as the 0 K value reported in ref 45.

TABLE 2: Results of Proton-Transfer Bracketing with Benzoylnitrene Radical Anion

reference acid	ΔG_{acid}[a]	proton transfer?[b]
malononitrile	1376 ± 8	yes
3-methylbenzoic acid	1395 ± 8	yes
1,2,4-triazole	1410 ± 8	yes
pyruvonitrile	1413 ± 8	yes
formic acid	1419 ± 8	yes
1,2,3-triazole[c]	1423 ± 8	no
1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol	1425 ± 8	no
diethylmalonate	1432 ± 8	no
imidazole	1434 ± 8	no
pyrrole	1468 ± 8	no
aniline	1502 ± 8	no
ethyl acetate	1527 ± 17	no
isopropyl alcohol	1542 ± 5	no

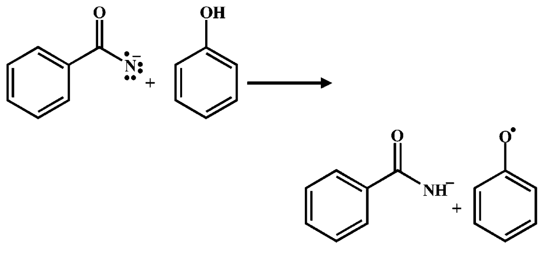
[a] Values taken from ref 36, in kilojoules per mole. [b] Indicates whether proton transfer is observed in the reaction of benzoylnitrene radical anion, **1**$^-$, with the reference acid. A "yes" indicates that proton transfer is observed; "no" indicates it is not. [c] Reference 28.

nitrogen positions in **1**$^-$, electronic structure calculations (B3LYP/6-31+G*)[19] predict that protonation at the nitrogen is more favorable by 12 kJ/mol, and it is presumed that benzamidyl radical, **2**, is formed upon protonation. Table 2 shows the results of proton-transfer reactions between ion **1**$^-$ and a series of reference acids (eq 6). The results indicate that the acidity (ΔG_{acid}) of **2** lies between those of formic acid (1419 ± 8 kJ/mol) and 1,2,3-triazole (1423 ± 8 kJ/mol),[28−30] and we assign $\Delta G_{acid}(\mathbf{2}) = 1421 \pm 10$ kJ/mol, where the uncertainty is chosen to cover the uncertainties in the acidities of formic acid and 1,2,3-triazole, and the acidity range between them. At the B3LYP/6-31+G* level of theory, the entropy difference between **1**$^-$ and **2** is calculated to be 1 J/(mol K), giving $\Delta S_{acid} = 108$ J/(mol K), such that $\Delta H_{acid}(\mathbf{2}) = 1453 \pm 10$ kJ/mol at 298 K.



(6)

Although the gas-phase acidities of phenols are similar to the acidity of **2**, they were not used in bracketing studies because they react with **1**$^-$ by hydrogen atom transfer, resulting in an ion corresponding to deprotonated benzamide (benzamidyl anion, **2**$^-$, eq 7). Ion **2**$^-$ is more basic than **1**$^-$ ($\Delta G_{acid}(\mathbf{3}) =$ 1452 ± 8 kJ/mol), and therefore its formation could lead to false positive results. None of the reagents shown in Table 2 undergo hydrogen atom transfer with **1**$^-$. By combining the enthalpy of formation of **1**$^-$ with the measured proton affinity we obtain $\Delta H_{f,298}(\mathbf{2}) = 110 \pm 14$ kJ/mol.



2$^-$

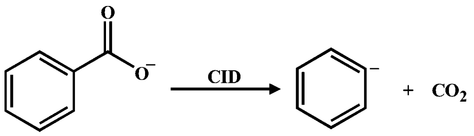
(7)

Discussion

The measured enthalpies of formation of **1**$^-$ and **2** can be used to calculate a variety of thermochemical properties. This section describes the thermochemical results and also compares them with values for analogous systems. As indicated in the introduction, ion **1**$^-$ resembles the benzoate ion, where one of the oxygen atoms has been replaced by nitrogen. The thermochemical properties for **1**$^-$ reflect the difference expected given the differences in the electronegativity between N and O.

The proton affinity of ion **1**$^-$ is measured to be 1453 ± 10 kJ/mol, slightly higher than the proton affinity of benzoate (1423 ± 9 kJ/mol).[31] The difference in proton affinities (30 ± 14 kJ/mol) just barely agrees with the difference of 17 kJ/mol calculated at the B3LYP/6-31+G* level theory. In comparison, radical **2** is more acidic than benzamide (Table 1) by 28 ± 13 kJ/mol, likely because the additional proton in **2**$^-$ effectively lowers the electronegativity of the nitrogen. Geometry differences are not expected to play an important role, as the N−H bonds in both **2** and **3** are calculated to be coplanar with the carbonyl.

The measured dissociation energy of benzoylnitrene radical anion is 0.82 ± 0.09 eV, which is significantly lower than the dissociation energy of 2.63 ± 0.15 eV for benzoate ion.[32] The large difference results because **1**$^-$ and benzoate anion dissociate to give different types of products. Whereas CID of **1**$^-$ results in formation of phenyl radical and NCO^-, dissociation of benzoate gives phenyl anion and neutral CO_2 (eq 8). Dissociation of **1**$^-$ to give phenyl anion and NCO radical requires 3.38 ± 0.10 eV, more similar to the dissociation energy of benzoate.



(8)

The measured enthalpy of formation of **1**$^-$ can be used to determine the homolytic N−H bond dissociation energy of benzamide (eq 3). By combining $\Delta H_f(\mathbf{2}) = 110 \pm 14$ kJ/mol with the enthalpy of formation of benzamide, −101 ± 1 kJ/mol (Table 1), the 298 K homolytic bond dissociation enthalpy of N−H in benzamide is found to be 429 ± 14 kJ/mol. This value is slightly lower than but is in reasonable agreement, within error, with that reported by Bordwell and co-workers for benzamide in DMSO solution, 448 kJ/mol.[7−9] In that work, the similarity between the BDE of benzamide and NH_3 was interpreted to indicate that the CO group does not stabilize the nitrogen-centered radical in the carboxamide, **2**. Because the amide is already planar with delocalized electrons,[33] the radical

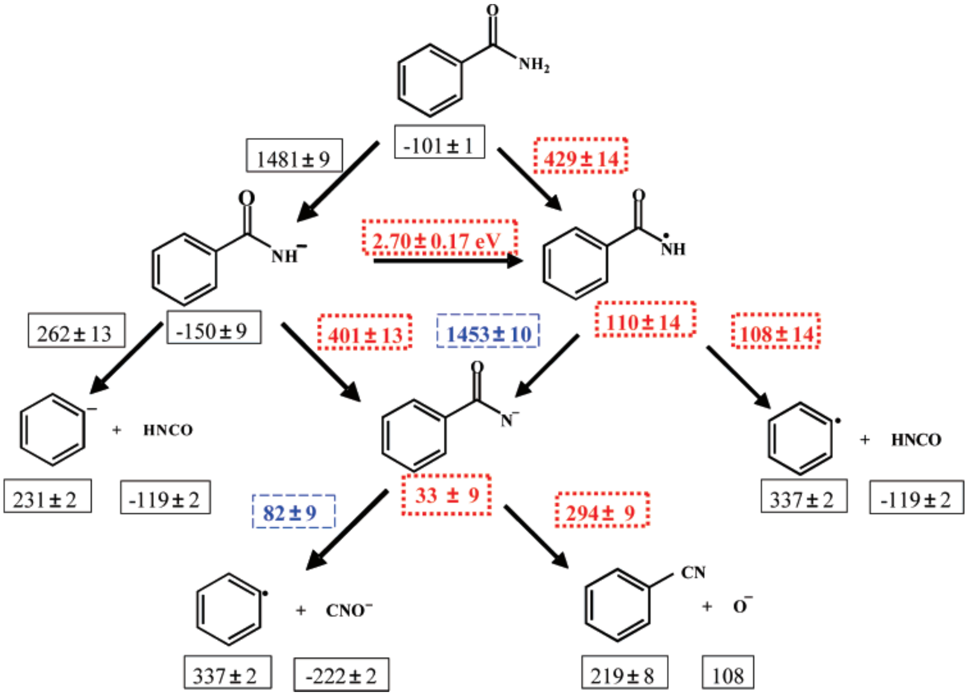


Figure 2. Additional thermochemical properties derived from the studies of benzoylnitrene radical anion. All values are in kilojoules per mole. Values in blue dashed-line boxes were measured directly in this work, whereas values in red dotted-line boxes were derived from those measurements and literature values, shown in black.

formed upon breaking the N−H bond is in the plane and not stabilized by delocalization. However, we note that this analysis does not account for the O−H BDE in acetic acid,[34] which is ca. 40 kJ/mol weaker than that in water. The BDE measured in this work is significantly lower than a recently reported computed value of 459 kJ/mol,[10] but the difference between the theoretical and experimental values (30 ± 14 kJ/mol) is comparable to the 16−20 kJ/mol difference between the computed[10] and experimental[7,8] N−H BDEs in acetamide.

Other quantities that can be derived from the measured enthalpies of formation of **1**$^-$ and **2** are shown in Figure 2 and include the following.

(1) Electron affinity of benzamidyl radical, **2**: The electron affinity of **2** can be calculated from the energy difference between **2** and **2**$^-$. The enthalpy of formation of **2**$^-$ is determined from the enthalpy of formation and gas-phase acidity of benzamide, **3** (Table 1). Assuming that the temperature correction is small, the quantity EA(**2**) is found to be 2.70 ± 0.17 eV. The electron affinity of the nitrogen-based radical is more than 0.6 eV lower than that for the corresponding benzoate radical (3.45 ± 0.16 eV),[35] which is likely, in part, due to the differences in electronegativities of N and O.

(2) HNCO binding energy of phenyl radical: The measured enthalpy of formation of **2** indicates that HNCO is weakly bound to phenyl radical, by 108 ± 14 kJ/mol. However, HNCO binds to phenyl radical much more strongly than does CO_2, which is bound by only 13 ± 12 kJ/mol in benzoate radical.[35,36]

(3) Hydrogen atom affinity of **1**$^-$: The enthalpy difference between **2**$^-$ and **1**$^-$ can be used to calculate the hydrogen atom affinity of **1**$^-$, which is the homolytic N−H BDE in **2**$^-$. The measured value of 401 ± 13 kJ/mol is slightly lower than the N−H BDE in benzamide, which can be attributed additional ion stabilization due to the higher electronegativity of N as opposed to NH. The electronegativity difference is less important in the neutral system.

(4) Oxygen anion affinity of benzonitrile: By using the enthalpies of formation of **1**$^-$ and benzonitrile, the oxygen anion binding energy in **1**$^-$ is found to be 294 ± 9 kJ/mol, suggesting that the benzoylnitrene radical anion (and presumably other nitrene anions) could, in principle, be formed by direct addition of O^- to nitriles under high-pressure conditions. However, addition products have not been reported in studies of O^- with nitriles,[37−40] suggesting that either there is a barrier for the addition or more favorable reaction pathways are possible. Alternatively, the high binding energy indicates that acylnitrene anions could be formed by reaction with a good O^- donor, such as CO_3^- ($\Delta H(O_2C{-}O^-) = 195 \pm 23$ kJ/mol).[41] An in situ synthesis of the ion would eliminate the need for using acylazides, which are potentially explosive, especially with low-molecular weight systems (such as acetylazide).

Conclusions

Two simple thermochemical measurements with benzoylnitrene radical anion have allowed the determination of a wide variety of thermochemical properties, including the N−H BDE in benzamide. Our measured BDE is slightly lower than that reported previously, but agrees with it within error. The other measured values follow patterns similar to those observed for the decomposition of benzoic acid, but with slight differences that can generally be attributed to electronegativity differences between nitrogen and oxygen. The energetics of benzoylnitrene radical anion suggest that it could be formed in situ by addition of O^- to benzonitrile, potentially providing a general synthetic method for this class of reactive ions.

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